STRUCTURAL STUDIES IN ALICYCLIC SYSTEMS

A thesis
submitted in partial fulfilment
of the requirements for the Degree
of
Doctor of Philosophy in Chemistry
in the
University of Canterbury

by

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University of Canterbury

1987

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ABSTRACT

The crystal structures of exo- (22) and endo- (23) adducts of tetracyclone and cyclopentadiene have been determined and the relative orientations of the four phenyl rings shown to be similar in the two structures.

The reactions between hemicyclone and a number of substituted benzoquinones gave a series of Diels-Alder adducts. Photolysis of the adducts gave derivatives of (21) and/or (29). Other reactions of the parent compound with various reagents were studied. The X-ray crystal structures of oxetane (29) and cyanohydrin (55) were determined.

The reactions of the diene (37) with twenty-two dienophiles have been studied and the stereochemistry of the products have been determined by crystallographic or spectroscopic means. With olefinic dienophiles reaction occurs exclusively by attack on the carbonyl-bearing face of the diene component of (37), whilst other dienophiles (benzyne, azo compounds and acetylenes) exhibit mixed π-facial selectivity. The origin of the mixed stereoselectivities is discussed. The X-ray crystal structures of the diene (62) and four Diels-Alder adducts (87), (90), (101) and (102) are discussed.

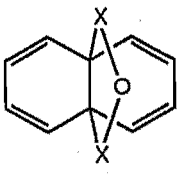
The Diels-Alder reactions between cyclopentadiene and a number of substituted benzoquinones gave a series of adducts. Reduction of these adducts and reaction with organometallic reagents were investigated. One- and two-dimensional n.m.r. analyses of selected products are discussed.

INTRODUCTION

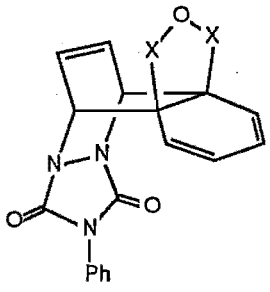
Cycloaddition reactions are of considerable importance in synthetic organic chemistry since they provide access to cyclic compounds from acyclic substrates. The earliest recorded cycloaddition reactions, the reaction of cyclopentadiene with simple quinones, were carried out by Albrecht[1] in 1906 but the results were not correctly understood until their reinvestigation by Diels and Alder[2,3] some twenty years later. Diels-Alder reactions involving cycloadditions of dienes to quinones have become key steps in the syntheses[4,5] of many important compounds including steroids and antibiotics. The application of the principle of conservation of orbital symmetry[6] in conjunction with the frontier orbital[7] and the Huckel/Mobius approach[8] lays the foundation for study in such systems. Woodward and Hoffmann's theory of pericyclic reactions[6] gained rapid acceptance because it gathered together a large body of chemical fact previously considered to be unrelated. Fukui's frontier orbital approach similarly provides insight into pericyclic reactions and Hoffmann and Fukui received the award of the Nobel Prize in recognition of their work, unfortunately after Woodward's death. In particular the general process in which dienophiles undergo cycloaddition to 1,3-dienes (the Diels-Alder reaction) is considered to be controlled by the in-phase compatability of frontier-orbital pairs (overlap of orbitals of like sign). These in-phase relationships, defined as first-order orbital interactions, are strongly favourable and constitute the major source of reaction stereospecificity.

Several aspects of cycloadditions, particularly stereoselectivity and regioselectivity, are controlled by

second-order orbital interactions. The frequently observed adherence of [$_{\pi}4$ + $_{\pi}2$] cycloadditions to the Alder rule of endo-addition is considered to arise from symmetry-allowed mixing of secondary reaction centres when the interacting species are endo-orientated.[6,9] These secondary effects can exert a major impact on the facial selectivity in cycloaddition reactions.[10] For example, the reaction between N-phenyl triazolinedione (PTAD) and the propellane (1) gave the product (3) only, whereas the corresponding reaction with the propellane (2) gives a product (4) of opposite stereochemistry. The primary



(1) X=CH_2
(2) X=CO



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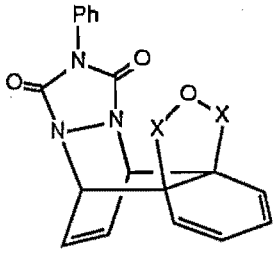


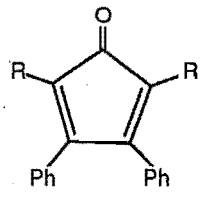
(4)

effect is present irrespective of whether the PTAD interacts with the diene from either face but a secondary orbital interaction between the π-system of the anhydride bridge and the n-orbitals of the azo group operates only in the case of compound (2).

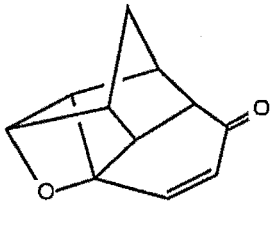
The work in Chapter 1 of this thesis examines the steric effect and orientation of phenyl rings in two Diels-Alder adducts of the tetrasubstituted dienone (5a). The presence of bridgehead substituents prevent the use of proton-proton coupling to differentiate exo- and endo-stereochemistry and in particular, phenyl substituents reduce secondary orbital effects in the transition state of the Diels-Alder reaction.

The addition of two alkenes to form a cyclobutane is a well established photochemical cycloaddition reaction. The earliest

recorded [$_{\pi}2$ + $_{\pi}2$] intramolecular cycloaddition involved the photolysis of a norbornadiene derivative[11] although the conversion of norbornadiene itself to quadricyclene was not effected until some years later.[12] Intramolecular cycloadditions generally yield highly strained products which are unobtainable by other routes. For example, the initial step in the synthesis of cubane[13] involved an internal cyclisation of a derivative of endo-dicyclopentadiene. Caged molecules such as the diketone **(6)** synthesised by Cookson[14] have become the subject of resurgent interest in recent years since they are considered to have potential for energy storage[15,16] (Scheme 1). Furthermore this pentacyclic compound, prepared by photolysis of the Diels-Alder adduct **(8)** has served as an intermediate in the synthesis[17-20] of a number of interesting polycyclic compounds, including natural products.



(5) a: R=Ph
b: R=CH_3

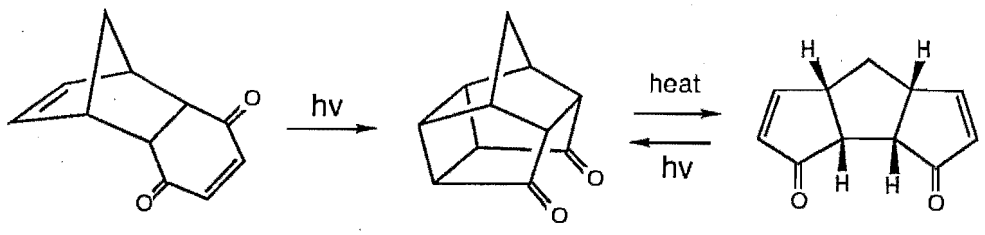


(9)

The formation of oxetanes was first reported by Paterno[21] in 1909 and the mechanistic features were first studied many years later by Büchi.[22] The Paterno-Büchi reaction is an oxa analogue reaction of a [$_{\pi}2$ + $_{\pi}2$] cycloaddition where a carbonyl compound adds to an alkene to form an oxetane. A potential side product of the photolysis of **(8)** shown in Scheme 1 is formation of the oxetane **(9)** which would result from [$_{\pi}2$ + $_{\pi}2$] cycloaddition involving either of the enedione carbonyl groups. The potential formation of oxetanes in systems where competing [$_{\pi}2$ + $_{\pi}2$] cycloadditions are possible would lower yields of the caged photoproduct and

hence careful modifications of these systems are necessary if a substrate is to be considered useful for storage of solar energy.

Scheme 1



(8) (6) (7)

A concerted mechanism[23,24] for the reaction of the n-π^* state of a carbonyl compound with an alkene is not expected because of the difficulty in obtaining appropriate orbital overlap in the transition state structure for the reaction. The n- and π^*-orbitals of the carbonyl group are orthogonal and overlap of these with the π/π^*-orbital of the alkene is geometrically difficult to achieve due to steric requirements. The Paterno-Büchi reaction is therefore considered to be a diradical process and proceeds by attack of singlet or triplet n-π^* state of the carbonyl compound on the alkene or by attack of the singlet or triplet state of the alkene on the carbonyl compound. The perpendicular approach of reactant molecules results in the formation of a carbon-oxygen σ-bond. The attack of excited carbonyl on alkene requires electron donating ability of the alkene since an electron on the π-orbital would be transferred to the n-orbital on the oxygen (Figure 1a). The alternative perpendicular approach mechanism would require electron donation from the n-orbital of the carbonyl to the molecular σ-orbital of the interacting system (Figure 1b).

For the π^*-orbital radical of the excited carbonyl to overlap effectively with the π-system of the alkene the substrates are required to be in a parallel configuration. The

symmetry allowed process[24] involves the transfer of an electron from the π^*-orbital of the carbonyl to the vacant π^*-orbital of the alkene, with formation of a carbon-carbon σ-bond (Figure 1c). This process is likely to occcur when the alkene is electron deficient. Carbon-oxygen σ-bond formation is a symmetry forbidden process[23,24] and can be ignored. The allowedness of photochemical reactions can in general be determined by construction of orbital correlation diagrams.[25,26] Transfer of an electron from the π^*-orbital of the alkene to the vacant π^*-orbital of the carbonyl is also possible via parallel approach of reactants (Figure 1d).

The work in Chapter 2 of this thesis enlarges on the chemistry of the Paterno-Büchi reaction and examines the effects of substitution and rotational hindrance on intramolecular cycloadditions.

The addition of reagents to the exo-face of norbornene (10) has been the subject of much interest and the general agreement is that stereoselectivities of these reactions are a result of the asymmetric arrangement of the allylic C-H and C-C bonds enforced by the rigid norbornene skeleton although the specific mechanism by which this asymmetric arrangement directs attack is controversial.[27] The face-stereoselectivities observed in Diels-Alder reactions of dienes fused to norbornane have been of interest since the addition of maleic anhydride to isodicyclopentadiene (11) by Alder et al.[28] in 1956. Diels-Alder reactions of (11) and its derivatives have since then been extensively studied by several workers.[29-35] Experiments have revealed that exclusive endo-face attack of (11) occurs with most dienophiles although adducts of mixed and exclusive exo-stereochemistry have been observed.[34] The reason for this

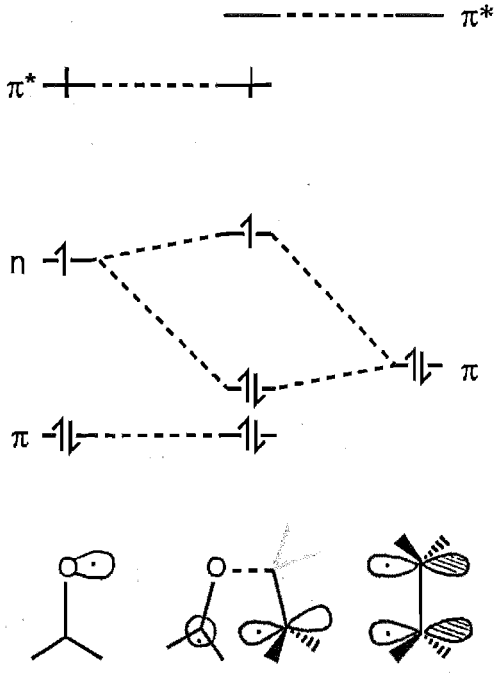


Figure 1a. The $\pi \longrightarrow$ n interaction for excited carbonyl (perpendicular approach).

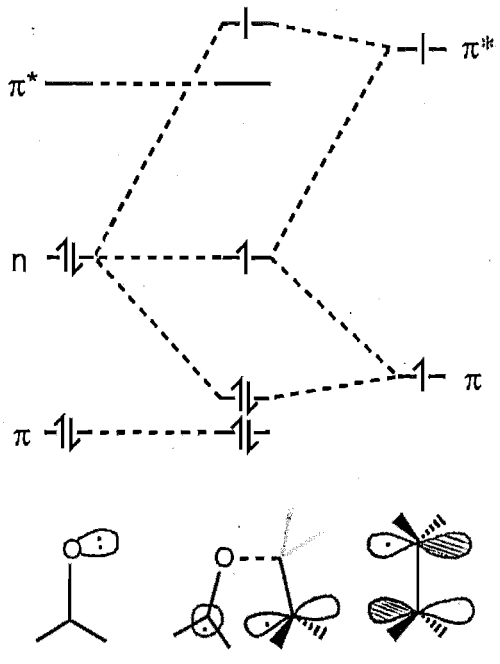


Figure 1b. The n $\longrightarrow$ π^* interaction for excited alkene (perpendicular approach).

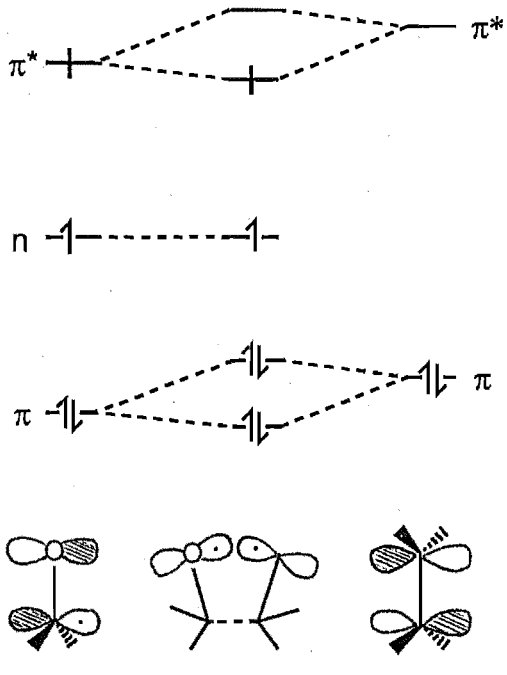


Figure 1c. The $\pi^* \longrightarrow$ π^* interaction for excited carbonyl (parallel approach).

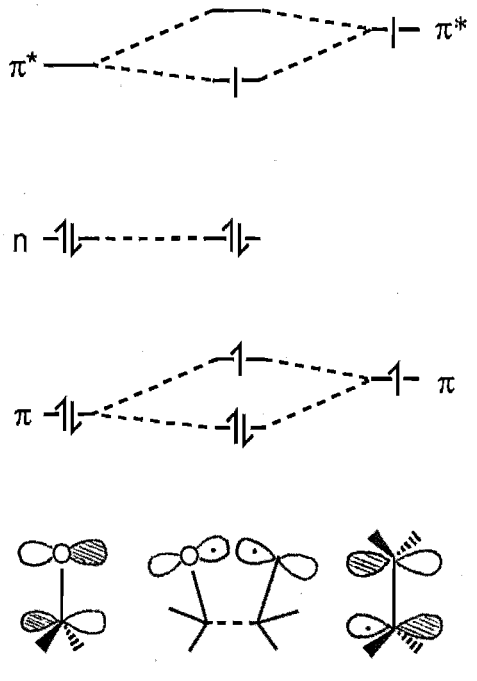
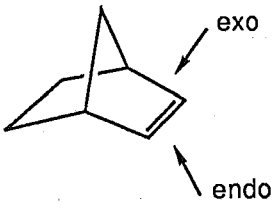


Figure 1d. The $\pi^* \longrightarrow$ π^* interaction for excited alkene (parallel approach).

behaviour must be an electronic rather than a steric one in the case of endo-addition as dienophile attack occurs on the same face as the larger ethano bridge but in the case of bulky dienophiles such as tetracyanoethylene (TCNE), there is a kinetic preference for exo-addition.[36] There has been considerable controversy as to the origin of the observed π-facial selectivities between dienophile attack on the top or bottom face of the diene component of (11) and several factors have been considered to explain the stereoselectivities of these reactions.



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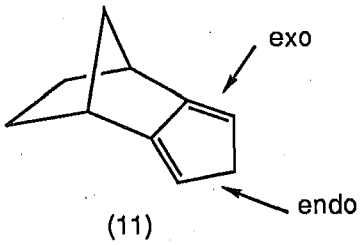

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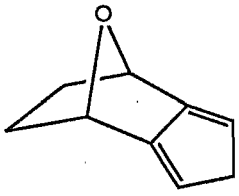


(12)

Vogel proposed that the stereoselectivitiy of cycloadditions of (11) and derivatives is determined by product stabilities.[30] That is, the factors that cause products resulting from endo-attack of dienophiles to be more stable than products resulting from exo-attack should also operate in the transition states for these cycloaddition reactions.

Polarizability effects[31] have been used to explain the selectivities observed for the reaction of reactive dienophiles, such as tetracyanoethylene, with the diene (12). In this case it is suggested that a charge transfer complex is established between the ethereal bridge of (12) and the incoming dienophile facilitating top-face attack.

The effect of π-orbital tilting associated with σ/π interactions has been suggested as a reason for preferred bottom-attack.[32] Molecular orbital calculations show significant differences in the frontier electron distribution on the exo- and

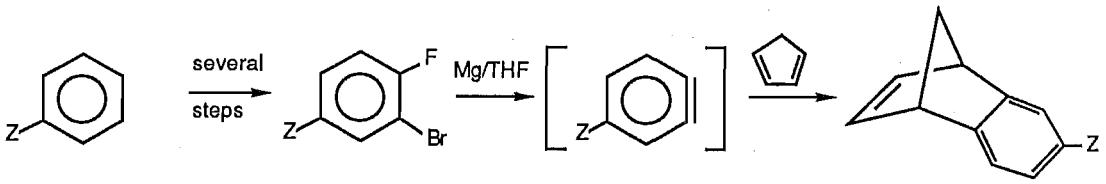
endo-diene surfaces and calculated energy differences of the two systems show that bottom-face attack is kinetically favoured.

Houk has suggested the origin of the selectivities to be a combination of torsional and steric effects.[33] The out-of-plane bending of groups at C2 and C3 of a diene in Diels-Alder transition states dictates the preferred direction of attack.

The work in Chapter 3 of this thesis is concerned with steric and electronic factors relating to the addition of dienophiles to a hexadiene ring fused to a polycyclic system.

The synthesis of benzonorbornadienes variously substituted in the benzene ring has been previously achieved by the reaction of the appropriately substituted benzyne with cyclopentadiene.[37] However the generation of such specifically substituted benzynes is not straightforward as indicated in Scheme 2 . In Chapter 4 an alternative approach to

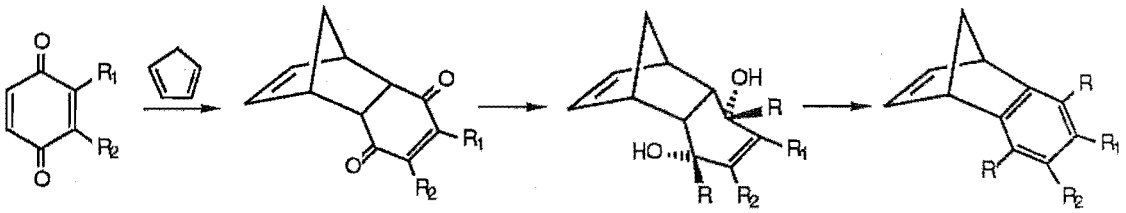
Scheme 2



benzonorbornadienes **(15)** is reported via dehydration of the diols **(14)**. Diols of this type should be accessible by reduction of, or addition of an organometallic reagent to, the Diels-Alder adducts **(8)** (Scheme 3). A synthesis has recently appeared for the preparation of the anthronorbornadiene **(15f)** via a similar sequence starting with the Diels-Alder adduct of 1,4-anthraquinone and cyclopentadiene.[38]

A systematic study of the reaction of quinones or enediones with organometallic reagents has not been reported in the literature. It appears that these reagents react to give very

Scheme 3

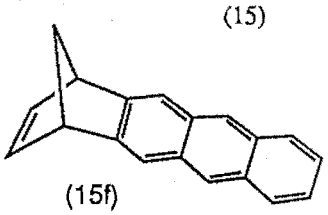


(13) (8) (14) (15)

a: $R_1=R_2=H$ d: $R_1=H$; $R_2=Bu^t$

b: $R_1=R_2=CH_3$ e: $R_1=R_2$=benzo

c: $R_1=H$; $R_2=CH_3$ R=H, CH_3, Ph



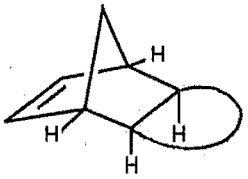
(15f)

complex reaction mixtures unless the quinone or enedione has suitable electron donating substituents.[39]

CHAPTER 1

PHENYL RING ORIENTATIONS IN TETRACYCLONE ADDUCTS

The [$_{\pi}4$ + $_{\pi}2$] cycloaddition of cyclopentadiene derivatives to cyclic dienophiles can produce exo- or endo-adducts (16) and (17) respectively, with the selectivity for these reactions frequently being controlled by secondary orbital interactions.[9,40] The assignment of stereochemistry to the



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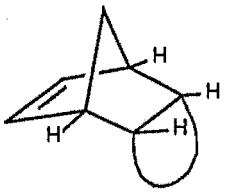

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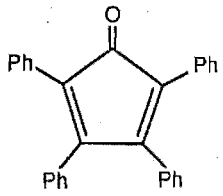
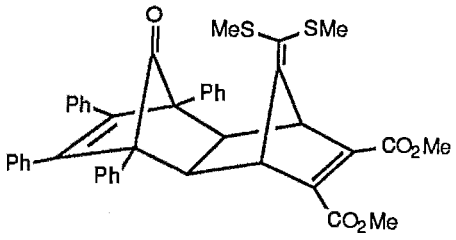


(5a)

adduct(s) is generally straightforward because of the greater coupling of the vicinal bridgehead protons in the ^{1}H n.m.r. spectra of the endo-adducts (17) compared with that in the exo-adducts (16). However, for adducts of 2,5-disubstituted cyclopentadienes the presence of bridgehead substituents precludes the use of this coupling to differentiate exo- and endo-stereochemistry.

Tetraphenylcyclopentadienone (tetracyclone) (5a) is an extensively used[41] reactive Diels-Alder diene and depending on the dienophile, can produce adducts with exclusively exo-,[42] exclusively endo-[43] or, more commonly, mixed stereochemistry. A number of physical methods have been explored to assign stereochemistry to such adducts, including ^{1}H n.m.r. solvent shifts,[44] lanthanide induced shifts[45] and ^{13}C n.m.r. chemical shift correlations.[46] Chemical methods[47] have also been used to assign stereochemistry. For example, the exo-stereochemistry of the tetracyclone adduct (18) follows from

its reductive conversion[42] to (19) whilst the endo-configuration of adduct (20) follows from its photolytic conversion[48] to the Cookson-type[14] cage structure (21).



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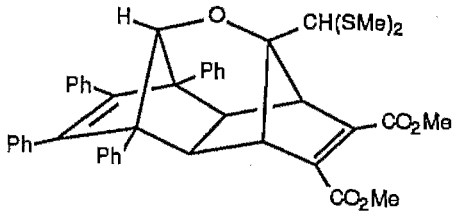
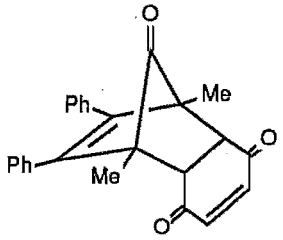


(19)

A study of a series of proton n.m.r. spectra of tetracyclone adducts suggested that the pattern of signals in the aromatic region may be related to stereochemistry of the adduct.[49] These



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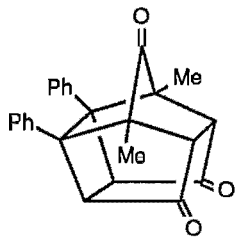
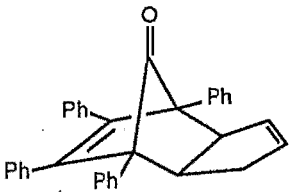


(21)

were classified on the basis that exo-adducts displayed two distinguishable resonances whereas endo-adducts displayed a multiplet signal only. It is reasonable to expect that the relative configuration of the adduct would influence the relative orientations of the phenyl rings and hence the appearance of the aromatic region of the spectrum. The tentative conclusions drawn from that study lead to difficulties as some pairs of adducts displayed essentially indistinguishable spectra.[50] The simplest way now available to establish configuration of adducts of this type is to consider $^{3}J_{C,H}$ coupling of the C5 and C6 protons with C7.[50,51] This method does however have some disadvantages since long accumulation times are required but it has been used to

reassign the stereochemistry of several tetracyclone adducts. Surprisingly no X-ray crystal structure of Diels-Alder adducts of tetracyclone had been reported so unambiguous crystal structure determinations were carried out for the two products obtained from the reaction of tetracyclone and cyclopentadiene. The adducts, **(22)** and **(23)**, are of interest since the phenyl groups are crowded and cannot exist in a coplanar arrangement with the ring double bond. Okamoto et al[52] suggested that phenyl crowding in the saturated adduct **(24)** results in elongation of the PhC-CPh bond (1.635 Å) by increasing the anti-bonding character of the occupied orbital by π-σ^* interaction. Hindrance to aryl rotation due to phenyl crowding is well established[53,54] and the activation parameters for aryl rotation in tetraarylcyclopentadienones have been measured.[53]



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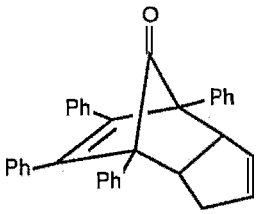

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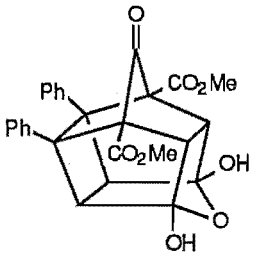
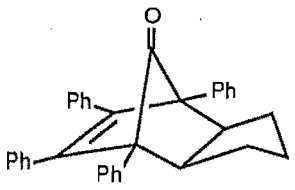


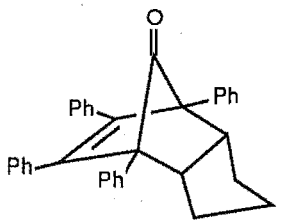
(24)

The reaction of tetracyclone with cyclopentadiene had been previously carried out by Grummitt et al[55] but these workers reported no evidence of the exo-isomer. Reaction of tetracyclone with a five molar excess of cyclopentadiene gave a mixture of two Diels-Alder adducts which were separated by fractional crystallisation. Integration of protons at δ 5.67 and 6.08 ppm in the olefinic region of the proton n.m.r. spectrum of the crude reaction mixture revealed the endo:exo product ratio to be 4:1. The stereoselective formation of the endo-adduct **(23)** can be ascribed to favourable secondary orbital interactions in the

transition state,[9] although the selectivity is less than that (97:3) reported[56] for the reaction between 2,5-dimethyl-3,4-diphenylcyclopentadienone (hemicyclone) and cyclopentadiene presumably due to the greater steric interactions in the former case. Hydrogenation of the adducts (22) and (23) gave the hydrogenated adducts (25) and (26) respectively. The ^{13}C n.m.r. spectra of the exo- (22) and endo- (23) adducts and the saturated analogues (25) and (26) confirmed the structural assignments reported by Mehta.[46]



(25)



(26)

The endo-adduct, unlike the parent analogue lacking phenyl groups, is resistant to thermal Cope rearrangement and instead undergoes a retro-Diels-Alder reaction.[54] The stereochemistry of (23) has however been established[51] by long range coupling of H2 or H6 with C10.

Figures 2 and 3 show perspective views and atom labelling of the exo- and endo-adducts (22) and (23) drawn in similar orientations. In the case of the exo-isomer (22) the position of the cyclopentenoid double bond is disordered in the two possible positions of the ring. As these diagrams show the relative orientations of the phenyl rings in the two adducts are remarkably similar and thus the orientation (exo- or endo-) of the fused ring does not significantly affect the phenyl ring conformations as had been previously assumed.[49]

Tables 1-3 list atomic coordinates, bond lengths and bond angles respectively for the two structures. Standard deviations

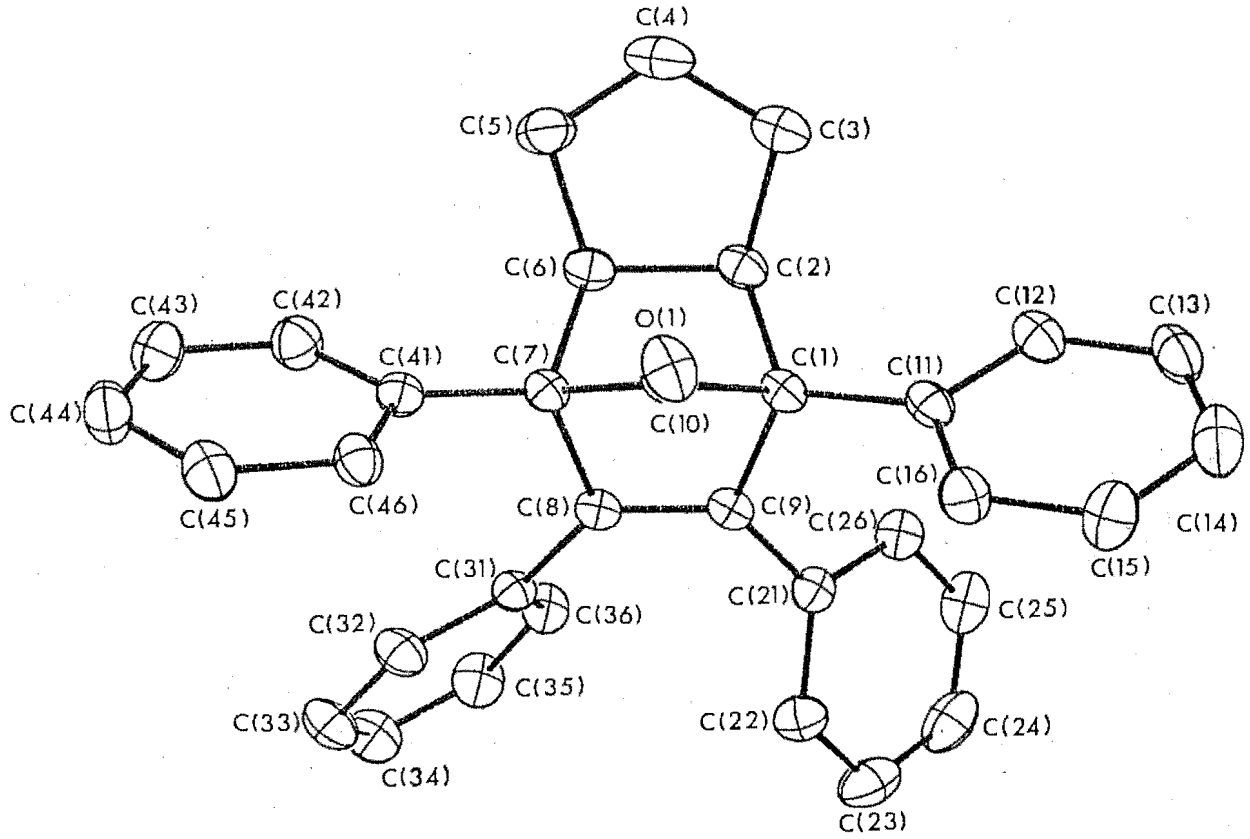


Figure 2. Perspective view and atom labelling of (22).
Hydrogen atoms omitted for clarity.

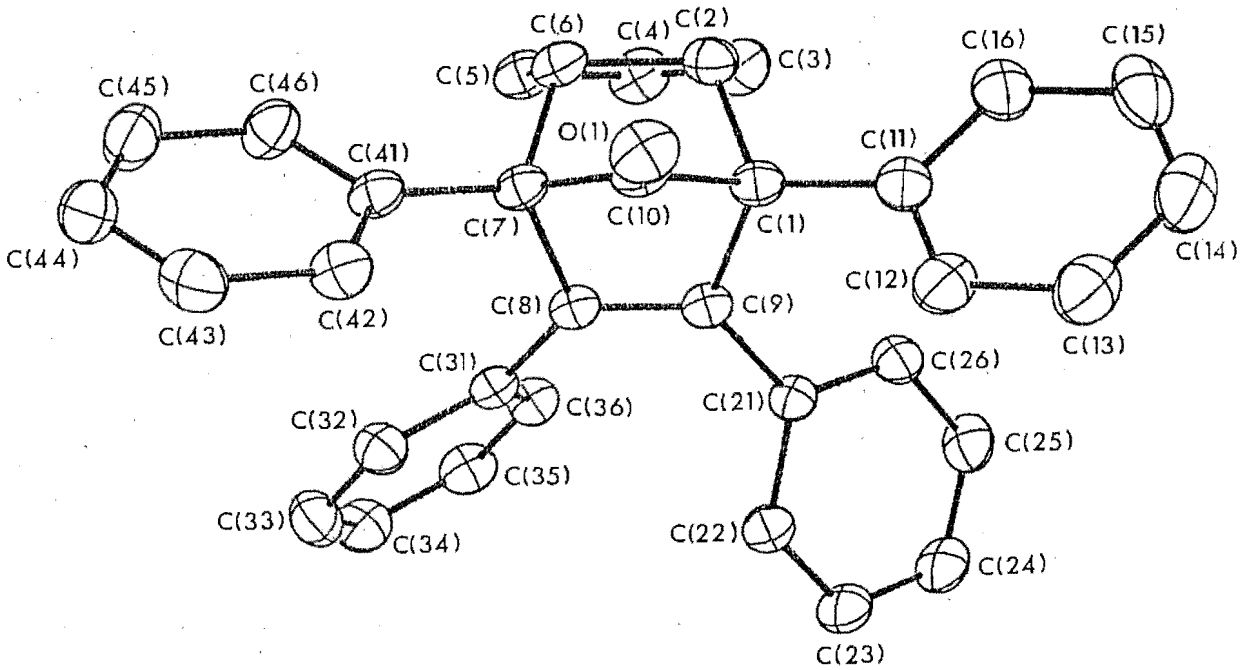


Figure 3. Perspective view and atom labelling of (23).
Hydrogen atoms omitted for clarity.

are given in parentheses. Corresponding bond lengths and angles are similar in the two structures. The C(8)-C(9) bond lengths (1.354 (2) Å for **(22)** and 1.355 (3) Å for **(23)**) are significantly longer than that reported[57] for the double bond of 1,2-diphenylcyclopentene (1.339 (7) Å) and for the corresponding bond in hemicyclone adducts[58,59], probably due to greater steric crowding exerted by the presence of bridgehead phenyl groups. The bonds attaching the bridgehead phenyl groups are longer than those attaching the phenyl groups to the double bond, indicating some conjugation of the latter phenyls with the double bond. The values of these bond lengths are similar to those attaching phenyl groups in similar environments in related structures.[58-65] In both structures all phenyl rings are planar to within 0.01 Å.

The orientations of the phenyl rings with respect to the plane described by C(1),C(7),C(8),C(9) are similar in the two structures. However in the exo-isomer **(22)** C(21) and C(31) both lie 0.14 Å on the endo-side of this plane whilst in the endo-isomer **(23)** C(21) lies in the plane and C(31) 0.267 Å below the plane. Furthermore it appears that steric interactions between the phenyl groups increase during the Diels-Alder reaction. For example the average non-bonded distance between ipso-carbons of adjacent phenyl groups in these two structures is 3.132 Å compared with an average value of 3.18 Å in 1,2,3,4-tetraphenylcyclopentadiene.[65] Non-bonded distances between ortho-carbons show even more marked increases in steric interactions. All intermolecular contacts between non-hydrogen atoms are >3.3 Å for both structures.

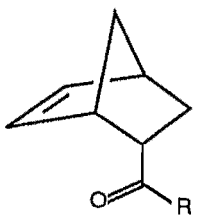
The fused cyclopentene rings are both planar with maximum deviations from the meanplanes being 0.016 Å and 0.009 Å for

(22) and **(23)** respectively. The bonds formed in the cycloaddition reaction (C(1)-C(2) and C(6)-C(7)) are all relatively long for C-C single bonds as is the case in a number of related structures. The C(1)-C(10)-C(7) bond angles indicate substantial strain about the carbonyl group which is also reflected in the infrared carbonyl stretching frequencies and the ease with which such compounds undergo decarbonylation reactions.[66]

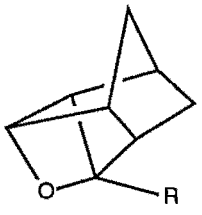
CHAPTER 2

THE CHEMISTRY OF HEMICYCLONE DIELS-ALDER ADDUCTS OF SUBSTITUTED BENZOQUINONES

Although formation of the oxetane **(9)** has not been observed, similar Paterno-Büchi reactions, eg. **(27)** to **(28)**, have been reported.[67-69] It has been reported[48] however that photolysis of the hemicyclone-benzoquinone Diels-Alder adduct **(20)** results in formation of the oxetane **(29)** in addition to the Cookson-type cage **(21)**. The structure of the highly strained oxetane **(29)** is of interest since it incorporates the theoretically interesting[70] tricyclo[3,3,0,$0^{3,7}$]octane (bisnoradamantane) skeleton **(30)**.



(27)



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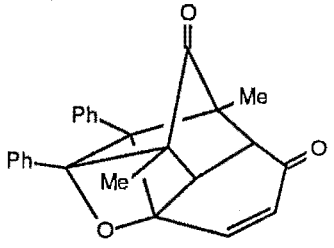
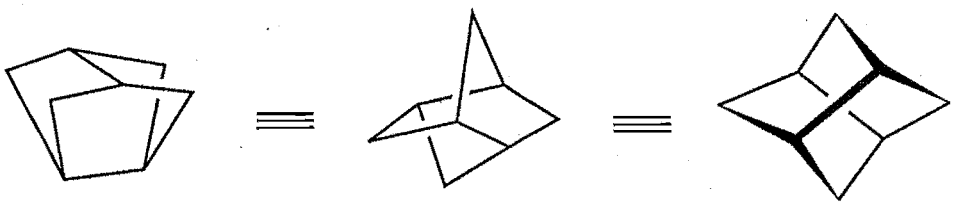


(29)



(30)

Photolysis of the hemicyclone-benzoquinone Diels-Alder adduct **(20)** gave a mixture of **(21)** and **(29)** as previously reported.[48] In order to confirm the structure of **(29)** and to examine the distortion of the bisnoradamantane skeleton present in this molecule a single crystal X-ray structure determination was undertaken. The two photolysis products were separated by

radial chromatography and the minor (30%) product was recrystallised from ethanol to give crystals suitable for X-ray crystallographic analysis. Figure 4 shows a perspective view with atom labelling of the pentacyclic oxetane **(29)**. Tables 4

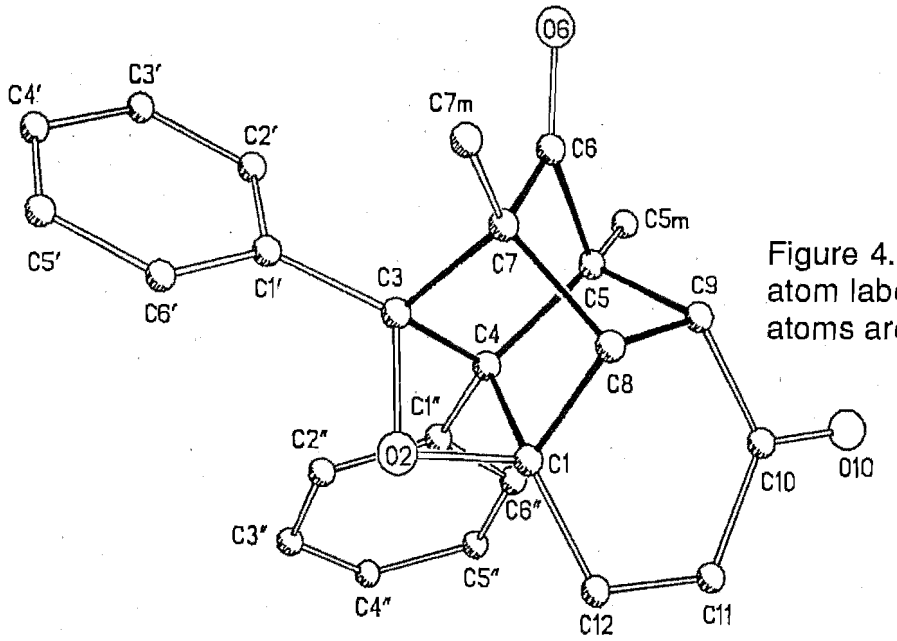


Figure 4. Perspective view and atom labelling of (29). Hydrogen atoms are omitted for clarity.

and 5 list bond lengths and angles with standard deviations in parentheses. The substantial strain present in this molecule is manifested in the bonding geometry. For example the bonds attaching C4 to C1,C3 and C5 are all > 1.575 Å, whilst the C1-C4-C3 bond angle (76.5°) is greatly distorted from the tetrahedral angle. Similarly the C1-C3 non-bonded distance (1.97 Å) is very short. These results contrast with those found for oxacyclobutane[71] (the simplest oxetane) where the C-C bond length is normal (1.534 Å). Also, the comparative bond angle (84.8°) in oxacyclobutane indicates the effect of substitution in **(29)**. The bisnoradamantane substructure present in **(29)**, and shown with highlighted bonds in Figure 4, is not significantly distorted from the D_{2d} symmetry[69] of the parent hydrocarbon, with the maximum deviation of any atom from the predicted position being < 0.1 Å. Whereas oxetane derivatives are normally close to

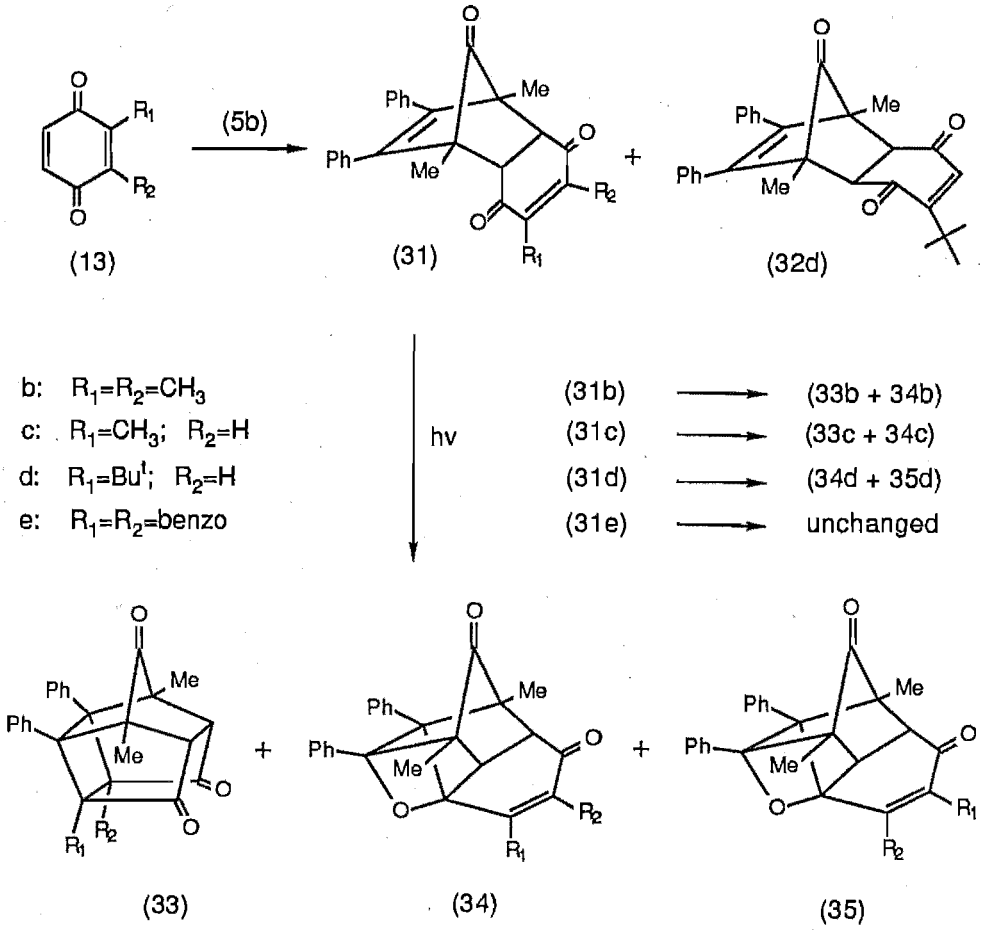
planar[71] the oxetane ring in **(29)** is severely puckered as measured by the angles of pucker between the C1-O2-C3 and C1-C4-C3 planes (41.8°) (c.f. 8.7° for oxacyclobutane) and between the O2-C3-C4 and O2-C1-C4 planes (45.6°). The phenyl rings are both planar to within 0.01 Å and inclined to one another at an angle of 77°. All intermolecular contacts between non-hydrogen atoms are > 3.0 Å.

Having established the structure of **(29)**, the effect of substituents and structure on the formation of such oxetanes was examined. Examination of molecular models suggested that the formation of the cage-adduct **(21)** might be less favourable in the presence of substituents on the double bond of the enedione precursor due to unfavourable steric interactions in the transition state of the $[_{\pi}2 + _{\pi}2]$ cycloaddition. Since electron withdrawing substituents in benzoquinone would be expected[72,73] to activate the substituted double bond in the initial Diels-Alder reaction it was decided to select electron releasing alkyl substituents in the benzoquinone starting compounds in order to ensure their correct location in the Diels-Alder adducts.

Thus reaction of the methylbenzoquinones **(13b,c)** with hemicyclone gave the Diels-Alder adducts **(31b,c)** with complete regioselectivity and endo-stereoselectivity (Scheme 4). The structures were assigned by spectroscopic comparison with related literature compounds.[41,46,48,74-77] In contrast tert-butylbenzoquinone **(13d)** gave a mixture of equal amounts of the endo- and exo-adducts **(31d)** and **(32d)**. These two isomers were separated by radial chromatography and distinguished by the relative postions of H2,H7 in the ^{1}H n.m.r. spectra and by similarity of chemical shifts in the ^{13}C n.m.r. spectra to that

of related compounds.[46] The formation of the exo-isomer in this latter reaction can be rationalized in terms of a steric interaction between tert-butyl and phenyl groups reducing

Scheme 4



secondary orbital stabilization[9,60,62] of the normal endo-transition state (Figure 5) which in turn allows competitive formation of the exo-product. The reaction of hemicyclone with 1,4-naphthoquinone (13e) produced the endo-isomer (31e) specifically.

Photolysis of the dimethyl adduct (31b) produced the cage compound (33b) and the oxetane (34b) in a 4:1 ratio indicating surprisingly little steric resistance to formation of the cage photoproduct (Scheme 4). A feature of the proton n.m.r. spectra of (34b) was the long range coupling (J 1.5 Hz) between the methyl protons at C11 and C12. In contrast photolysis of the

tert-butyl compound (31d) did not give any detectable [$_{\pi}2$ + $_{\pi}2$] cycloaddition product (33d) but gave a 3:1 mixture of oxetanes (34d) and (35d), separated by radial chromatography. These two

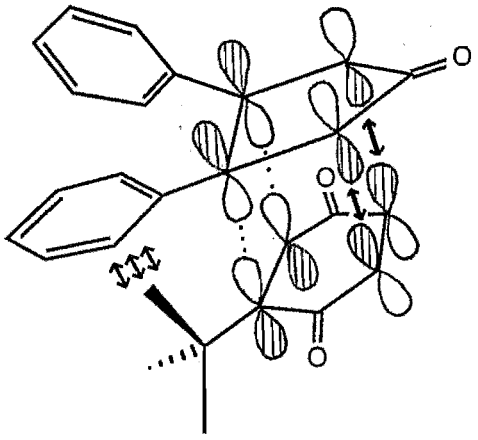
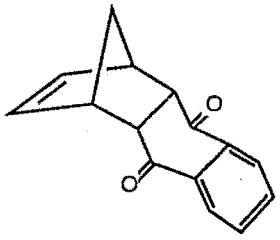


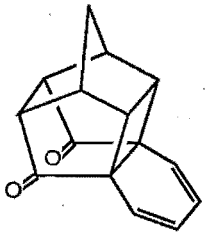
Figure 5. Steric interactions between t-butyl and phenyl groups reducing secondary orbital stabilisation of the normal *endo*- transition state.

isomeric oxetanes were distinguished by comparing the position of the enone protons with those protons in the proton n.m.r. spectra of oxetane (29). The ^{1}H n.m.r spectrum of the less polar isomer gave a singlet at δ 7.43 ppm whereas the corresponding spectrum of the more polar isomer gave a doublet at δ 6.15 ppm. As is the case for (29) the proton H11 displays a small coupling (J 1.0 Hz) to H9 whilst H12 displays no long range coupling, hence the former oxetane, exhibiting a singlet at δ 7.43 ppm was assigned as (35d) and the latter oxetane, exhibiting a multiplet at δ 6.15 ppm, was assigned as (34d). The absence of formation of (33d) is considered to result from a steric interaction between tert-butyl and phenyl groups preventing cyclobutane ring formation.
Photolysis of the monomethyl Diels-Alder adduct (31c) produced the expected cage product (33c) and, identified as above, the oxetane (34c) in a 3:1 ratio. The two products were separated by fractional crystallisation and identified by their ^{1}H and ^{13}C n.m.r. spectra. The less sterically congested oxetane isomer (35c) is not formed. Selective formation of (34c) and not (35c) can be explained either by selective excitation or greater

interaction of the frontier orbitals[72] of the carbonyl adjacent to the methyl with the stilbene π-system.



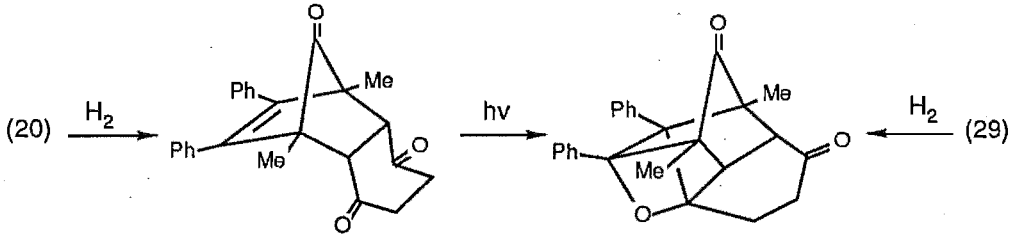
(36)



(37)

The naphthoquinone adduct (31e) was stable to photolysis. Annelation with the benzene ring sufficiently changes the energy of the frontier molecular orbitals to prevent formation of either cage or oxetane products. This contrasts with the cyclopentadiene-naphthoquinone adduct (36) which is converted photochemically[78,79] to the hexacyclic cage compound (37).

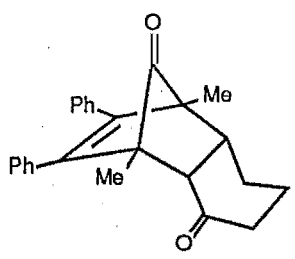
Scheme 5



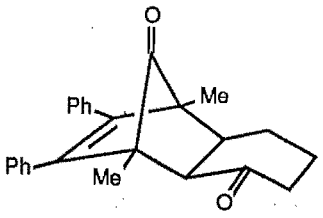
(38) (39)

In order to completely suppress formation of the cage products the enedione double bond was removed. Thus hydrogenation of (20) gave the reduced dione (38) which on photolysis gave the oxetane (39) in high yield (Scheme 5). The structure of (39) was confirmed by hydrogenation of the oxetane (29). The formation of (39) from dione (38) demonstrates that the presence of the enedione chromophore is not a requirement for oxetane formation.

Reaction of cyclohex-2-eneone with hemicyclone gave a mixture of endo- and exo-isomers **(40)** and **(41)** (ratio 5:4) which were separated by fractional crystallization. The isomers were



(40)



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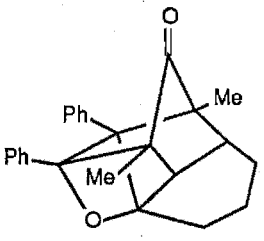
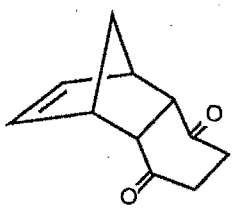


(42)

readily identified by preliminary photolysis experiments carried out on a mixture of the isomers. Examination of proton n.m.r. spectra showed that the methyl resonances at δ 1.37 and 1.48 ppm gradually disappeared whilst those at δ 1.17 and 1.27 ppm did not decrease in intensity. The appearence of methyl resonances at δ 0.90 and 1.30 ppm indicated the formation of an oxetane. Competitive formation of the exo-isomer can again be rationalized by the absence of secondary orbital stabilization of the endo-transition state. Photolysis of a sample of pure endo-isomer **(40)** resulted in the formation of oxetane **(42)** in high yield.

As noted earlier photolysis of **(8a)** does not produce the oxetane **(6)**, therefore removal of the enedione double bond might result in photochemical oxetane formation since competing cage formation would be impossible. Thus the enedione double bond of **(8a)** was selectively reduced using the method of D'Auria et al[80] to give dione **(43)** plus a small amount of the known[81] compound **(44)**. However photolysis of **(43)** gave a complex mixture of products rather than the desired oxetane **(45)**. Recently Wilson[82] reported that irradiation (360 nm) of **(44)** for 10-20 days produced a 10% yield of the oxetane **(46)** in addition

to the cage compound **(6)** and that the bis-adduct **(47)**, obtained from the reaction of tetrafluorobenzoquinone and cyclopentadiene, underwent photolysis in good yield to give a single product **(48)**.



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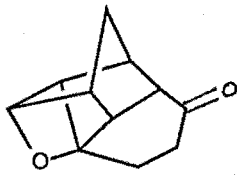

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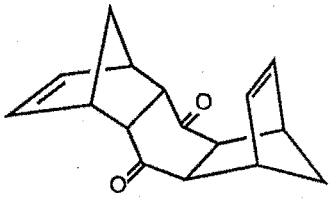

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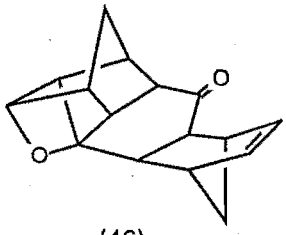

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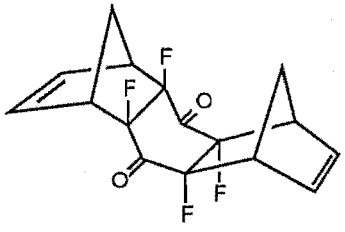

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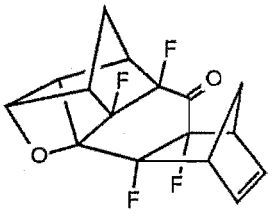
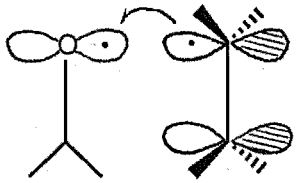
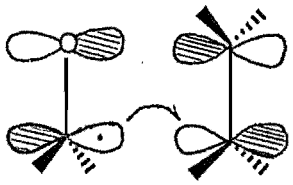


(48)

The efficiency with which the ketone **(47)** undergoes photolysis compared with the ketone **(44)** appears to be due mainly to electronic factors.



perpendicular approach
($\pi \longrightarrow$ n interaction)



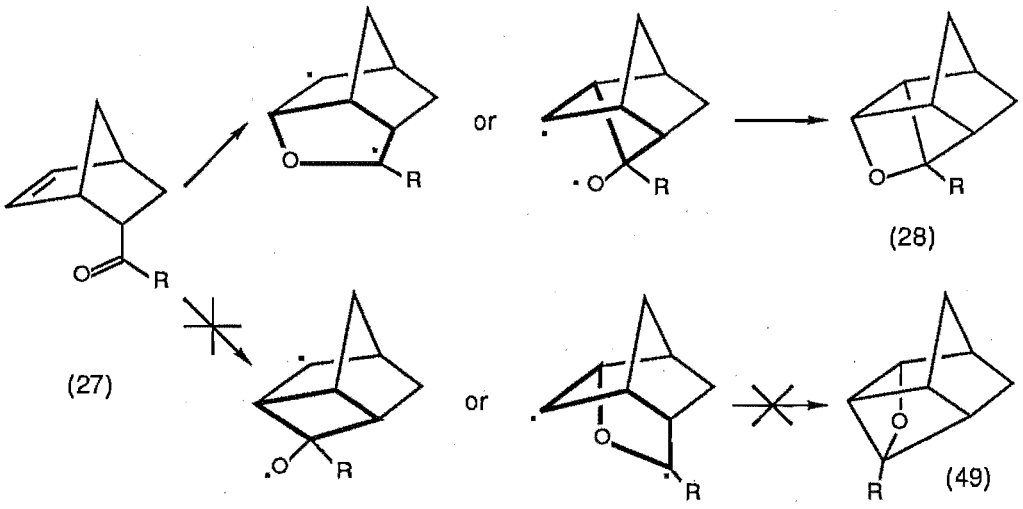
parallel approach
($\pi^* \longrightarrow \pi^*$ interaction)

Figure 6. Perpendicular or parallel approach of the two sets of interacting orbitals.

Several mechanisms have been considered[24] for the formation of oxetanes in the Paterno-Büchi reaction. These mechanisms involve either parallel or perpendicular approach of the two sets of interacting orbitals (Figure 6). Product formation can result from either σ-interaction between the first excited state of the enedione group and the ground state of the stilbene moiety or by interaction of the first excited state of the stilbene moiety with the ground state carbonyl. The photochemical reactions

performed in this thesis were carried out in benzene solutions in quartz reaction vessels. The use of a pyrex filter screens wavelengths below 290 nm hence direct excitation of the double bond of the stilbene moeity is unlikely although it may be possible for energy to be transfered to this bond from the excited carbonyl chromophore (inter- or intramolecular sensitisation). Of the symmetry allowed processes[24] perpendicular approach of the interacting groups requires overlap between the singly occupied n-orbital of the oxygen atom with the stilbene π-system. In contrast parallel approach of the interacting groups requires overlap of the antibonding π-orbital of the carbonyl carbon with the stilbene π-system.

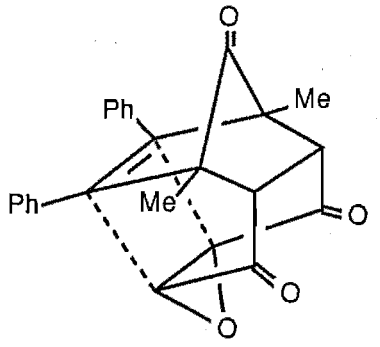
Scheme 6



For ketone (27) the rotational mobility of the carbonyl group allows for overlap of either the singly occupied oxygen n-orbital or the antibondinding π-orbital of the carbonyl with the stilbene π-system. Interestingly the alternative mode of Paterno-Büchi reaction to give (49) has not been reported to occur (Scheme 6). This is consistent with the empirical "rule of five"[24] since both of the allowed modes of formation of

(28) involve the formation of a five-membered ring in the diradical intermediate whereas the alternative mode of reaction requires formation of a four- or six-membered ring in an initial step (Scheme 6). For ketones (38) and (40) the constraints imposed by the additional six-membered ring are such that the oxygen n-orbital is now poorly aligned for overlap with the stilbene π-system. In the enediones (31b-d) the additional geometrical constraints in the ground state conformation similarly prevent any efficient overlap of the oxygen n-orbital with the π-system. It seems most likely therefore that for (31b-d), (38) and (40), oxetane formation results from parallel overlap of the π-systems but with considerable geometrical deformation from the ground state structure being required.

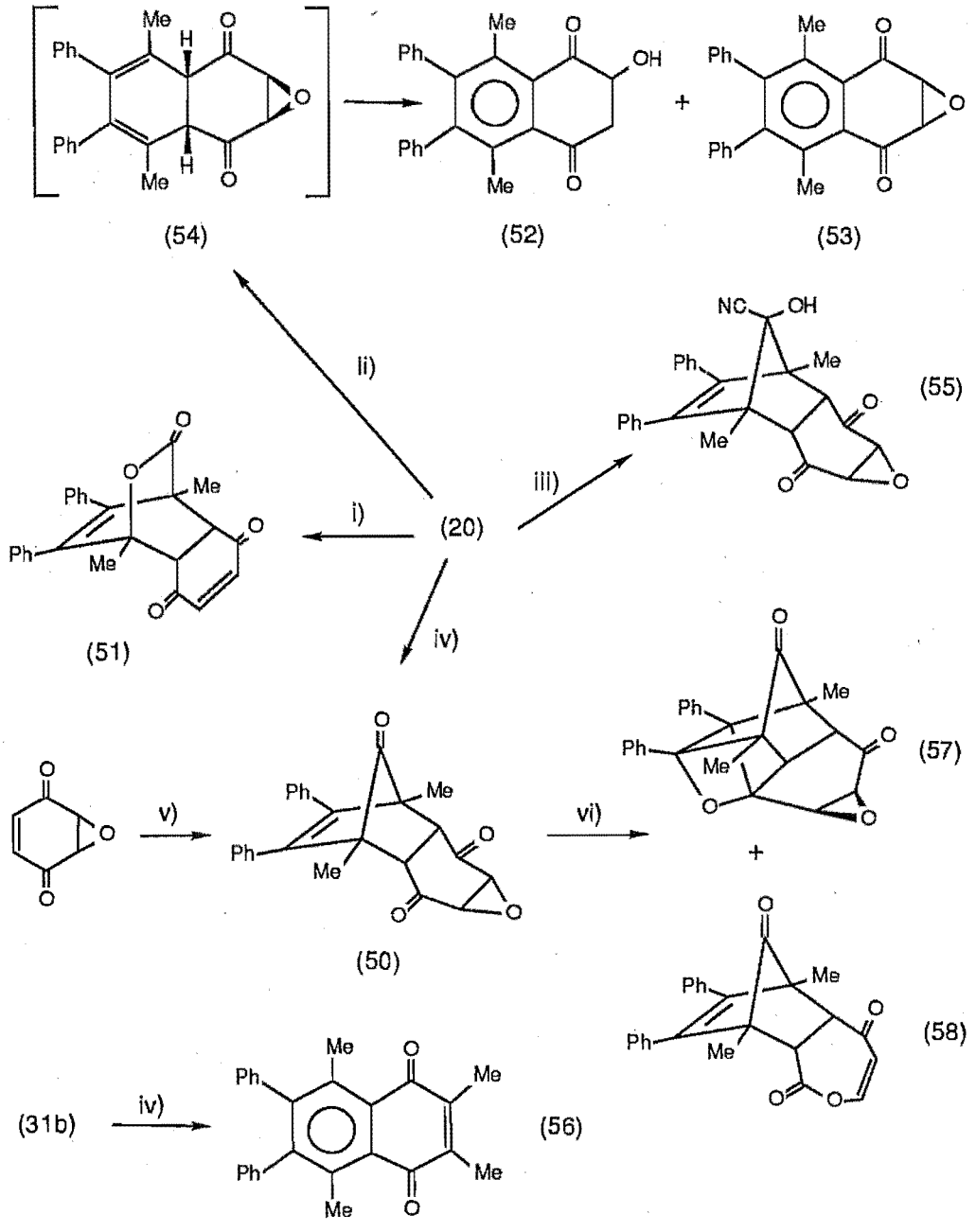
Figure 7. An intramolecular cycloaddition between an alkene and an epoxide ring.



Given the ease with which the intramolecular $[_{\pi}2 + _{\pi}2]$ cycloaddition occurs in systems of this sort it was decided to examine the possibility of effecting an intramolecular $[_{\pi}2 + _{\sigma}2]$ cycloaddition between an alkene and epoxide ring as shown in Figure 7. Intermolecular $[_{\pi}2 + _{\sigma}2]$ reactions are photochemically allowed and known.[83] Intramolecular $[_{\pi}2 + _{\sigma}2]$ cycloaddition of a π-bond to a strained cyclopropyl σ-bond is known[84] but cycloaddition to an epoxide carbon-carbon σ-bond is unknown. A cage skeleton related to the product that would result in the above $[_{\pi}2 + _{\sigma}2]$ reaction has in fact been reported[85] in an

acid-catalysed rearrangement reaction. Synthesis of the epoxide (50) was, however, not straightforward (Scheme 7).

Scheme 7



Reagents: i), m-chloroperbenzoic acid; ii), H_2O_2/20% K_2CO_3; iii), same as ii) plus TCNE; iv), H_2O_2/5% K_2CO_3; v), hemicyclone; vi), hv.

Attempted direct epoxidation of the enedione (20) with meta-chloroperbenzoic acid gave in high yield the Baeyer-Villiger product (51) which was identified by spectroscopic means. Similarly, attempted epoxidation with hydrogen peroxide and 20%

potassium carbonate gave the two decarbonylated products (52) and (53) which were isolated and identified by spectroscopic comparison with related literature compounds.[86,87] These two products are assumed to be formed from the unstable decarbonylated intermediate (54) which undergoes base-catalysed rearrangement to the hydroxydione (52) and oxidation to the epoxydione (53). An attempt was made to prove the intermediacy of the diene (54) by carrying out the oxidation reaction in the presence of tetracyanoethylene in the hope of trapping the diene as its Diels-Alder adduct. This resulted however in the formation of a cyanohydrin whose structure was confirmed by single crystal X-ray crystallography as (55).

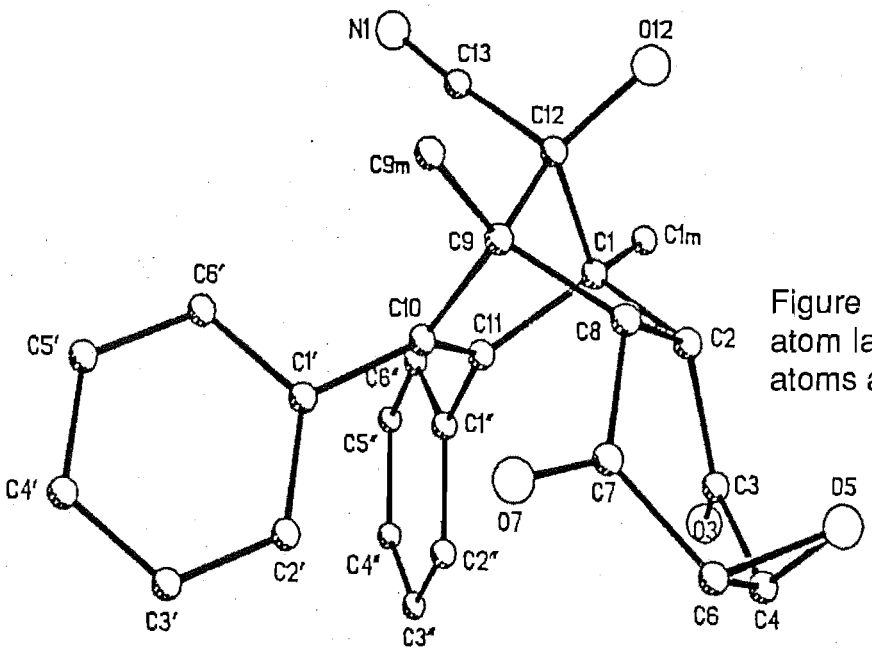


Figure 8. Perspective view and atom labelling of (55). Hydrogen atoms are omitted for clarity.

Crystals of (55) suitable for X-ray crystallography were obtained by recrystallisation from methanol; however these rapidly decomposed at room temperature due to loss of solvent of recrystallisation. Consequently the X-ray intensity data were collected at 133 K, at which temperature only minimal (5%) crystal decomposition occurred. The crystal used was however highly mosaic in one direction. Figure 8 shows a perspective

view and atom labelling of (55). Bond lengths and angles are listed in Tables 7 and 8, with standard deviations in parentheses, and are in agreement with those expected by comparison with related literature structures.[58,59,88,89] The phenyl rings are both planar to within 0.01 Å,&are inclined to one another at an angle of 92° and to the stilbene double bond plane at angles of 70.3° and 77.0°. This latter small torsional angle difference is the only significant feature which destroys the non-crystallographic mirror symmetry of the molecule. The epoxydione cyclohexane ring exists in a boat conformation with C3 and C7 0.4 Å below the plane described by C2,C4,C6 and C8. It is interesting to note that this is the conformation (B) proposed[90,91] to exist in the equilibrium shown in Figure 9 and that it brings the carbonyl groups closer to the stilbene π-system than the epoxide C-C bond. In the structure of (55)

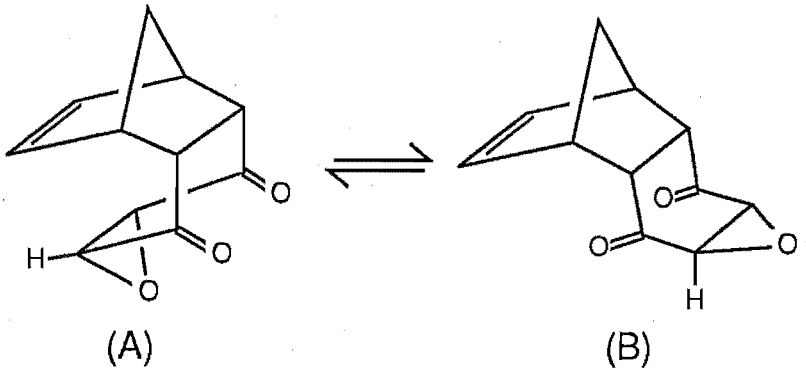


Figure 9. Equilibrium showing relative orientations of the carbonyl groups.

the two carbonyl oxygen atoms are only 3.2 (1) Å from the carbons of the stilbene double bond. The crystal structure of (55) also contains a methanol molecule in the asymmetric unit. The methanol acts as a hydrogen-bonding bridge linking molecules of (55) about a crystallographic centre of inversion as shown in Figure 10. All other intermolecular contacts between non-hydrogen atoms are > 3.1 Å.

The cyanohydrin formation is considered to result from base-catalysed decomposition[92] of tetracyanoethylene. It is

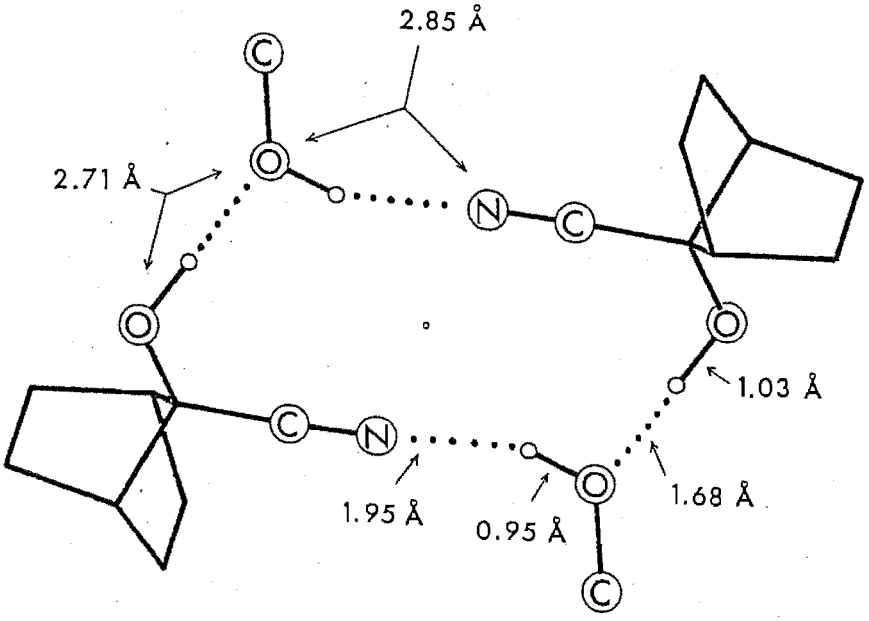


Figure 10. Intermolecular hydrogen bonding of (55).

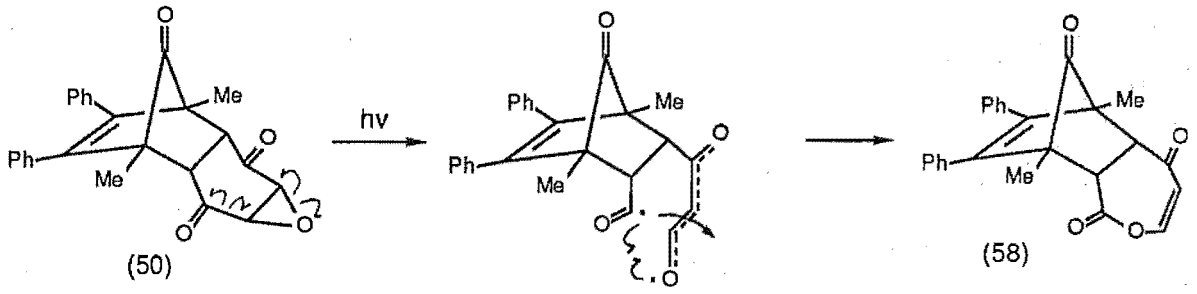
noteworthy that cyanide attack occurs exclusively on the face of the carbonyl group directed towards the stilbene group. The cyanohydrin serves to protect the bridging carbonyl group from decarbonylation and epoxidation of the enedione occurs on the more exposed exo-face of the enedione double bond.

The epoxide **(50)** was finally obtained (Scheme 7) by lowering the concentration of base (5% carbonate) in the epoxidation reaction of **(20)**. The epoxide **(50)** was also formed in the Diels-Alder reaction between hemicyclone and benzoquinone epoxide (itself prepared by a retro-Diels-Alder reaction[93] of its dimethylfulvene adduct) in addition to a small amount (ca. <10%) of a minor isomer. Epoxidation of adduct **(31b)** with hydrogen peroxide and 5% potassium carbonate (Scheme 7) gave the 1,4-naphthoquinone derivative **(56)**, identified by spectroscopic means, and not the expected epoxide. This result contrasts with the straightforward epoxidation of the adduct formed from the reaction of cyclopentadiene and 2,3-dimethylbenzoquinone.[94] It

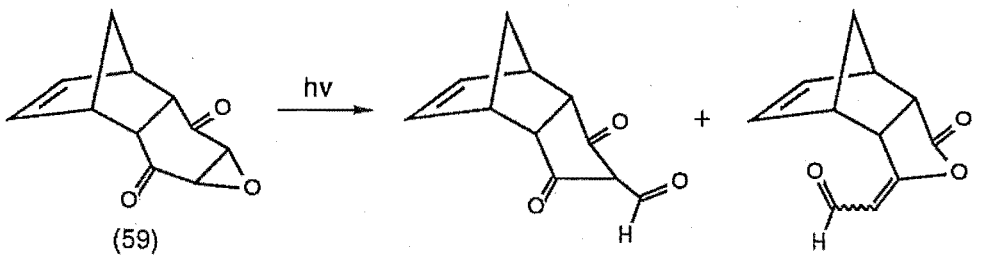
appears that the steric effect of the methyl groups in the enedione system create a significant energy barrier towards peroxide attack, whereas decarbonylation appears to require a lower energy pathway and occurs quite readily in the case of (31b).

Photolysis of the epoxide (50) under similar conditions to those used above gave a mixture of three products. Attempts to isolate and identify one of these photoproducts were unsuccessful. However a second product was identified as the oxetane (57) which is formed by a [$_{\pi}2$ + $_{\pi}2$] cycloaddition similar to those discussed above. The third product was identified by spectroscopic means as the unsaturated lactone (58) whose formation can be rationalised as shown in Scheme 8.

Scheme 8



Scheme 9

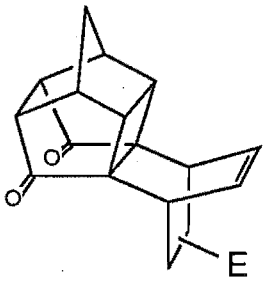


Although similar reactions have been reported[95] for α,β-epoxyketones the reaction course differs from that observed[96] for the closely related epoxydione (59) (Scheme 9).

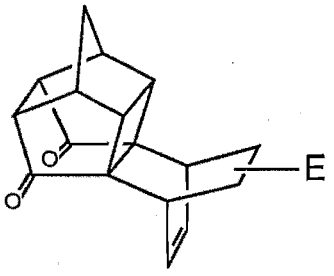
CHAPTER 3

PI-FACIAL SELECTIVITY IN DIELS-ALDER REACTIONS OF A POLYCYCLIC DIENE

A study of the Diels-Alder reactions of the diene (37) with several dienophiles was undertaken. The diene (37) is essentially a 1,3-cyclohexadiene ring fused to a Cookson-type cage.[14] This diene can undergo dienophile attack on either the carbonyl bearing face of the diene to produce (60), or on the opposite face to produce (61). Although three Diels-Alder



(60)

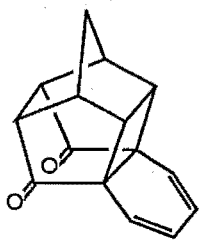


(61)

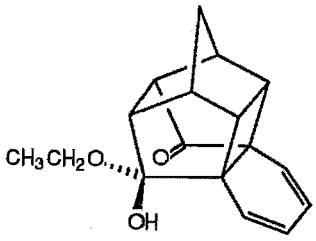
reactions of this diene had been previously reported[78,79,97-99], the stereochemistries of the adducts were ambiguous or as has turned out incorrectly assigned. In this chapter the determination of product stereochemistry, X-ray crystal structures of (62) and selected products, and the observed π-facial selectivities in the cycloaddition reactions are discussed.

The diene (37) was prepared according to the literature procedure[79] by photolysis of the Diels-Alder adduct from cyclopentadiene and p-naphthoquinone. Recrystallization of (37) from ethanol resulted in its conversion to the crystalline mono-hemiacetal (62), an X-ray crystal structure[100] of which is described below. In solution however, proton n.m.r. studies showed that (62) rapidly redissociates to the diene (37) and

ethanol. In the Diels-Alder reactions described below trial studies showed that the same products were obtained whether (62) or unrecrystallized (37) was used as starting material.



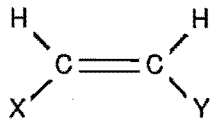
(37)



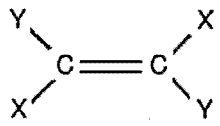
(62)

The various dienophiles used for reaction with (37) are listed in Chart 1. Table 10 summarizes the reaction conditions and product ratios for the Diels-Alder reactions. The diene (37) reacted smoothly, albeit slowly, with a variety of dienophiles to produce the Diels-Alder adducts (60) and/or (61). Product ratios were determined by 300 MHz ^{1}H n.m.r. spectral analysis of the crude reaction mixtures. The stereochemistry of the adducts was determined by a variety of methods: X-ray crystallography[100,101] or by spectroscopic or chemical means. Nuclear Overhauser effect difference (NOED) spectroscopy[102] proved particularly useful for distinguishing between (60) and (61), since spin-spin coupling information is not transmitted through the "spectroscopically silent" propellane carbons of the adducts. A typical example is shown in Figure 11. The normal 300 MHz proton n.m.r. spectrum of the benzoquinone adduct is shown in Figure 11a along with the proton assignments, which were determined on the basis of homonuclear decoupling and NOED experiments. The NOED spectrum resulting from irradiation of the olefinic protons H_x is shown in Figure 11b. This spectrum shows significant enhancement of the signals due to the spacially proximate protons, H_p and H_c. Similarly, irradiation of

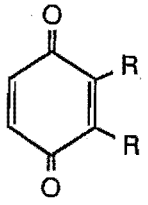
Chart 1



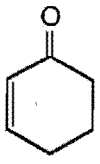
(63) X=H, Y=COMe
(64) X=H, Y=CO_2Me
(65) X=H, Y=CO_2H
(66) X=H, Y=CN
(67) X=H, Y=OAc
(68) X=Y=CO_2Me



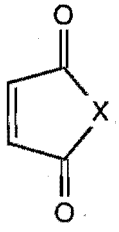
(69) X=H, Y=CO_2Me
(70) X=Y=CN



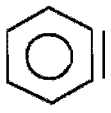
(13a) R=H
(13b) R=CH_3
(13e) R=benzo



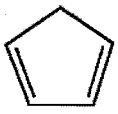
(73)



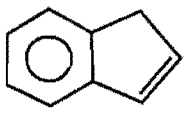
(71) X=O
(72) X=NPh



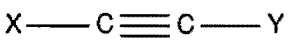
(74)



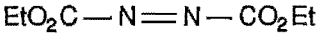
(75)



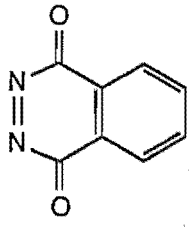
(76)



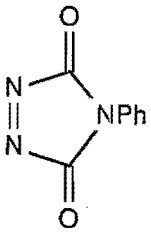
(77) X=H, Y=CO_2Me
(78) X=Y=CO_2Me



(79)



(80)



(81)

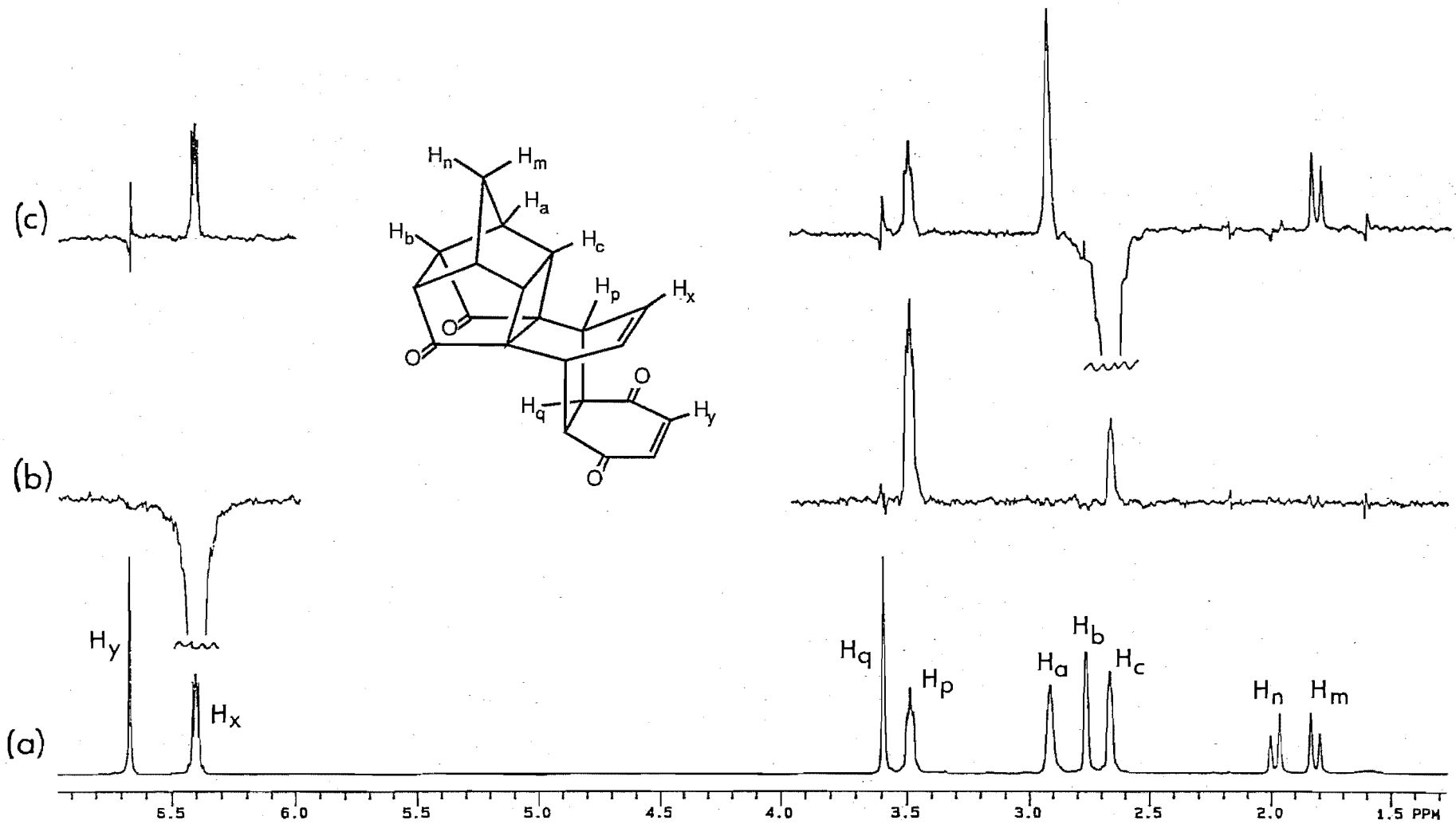
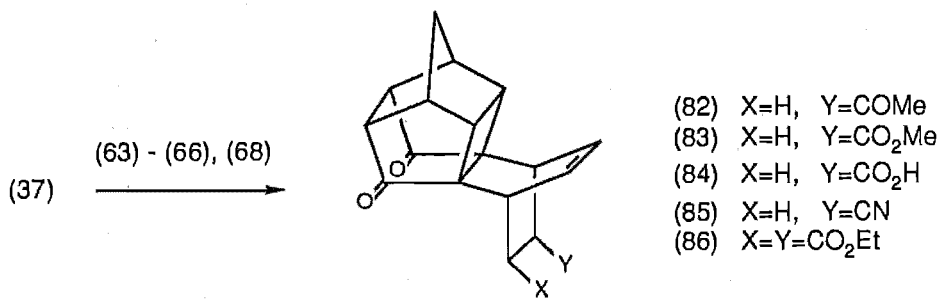


Figure 11. Normal ^1H n.m.r. spectra (a) and NOE difference spectra (b,c) for the benzoquinone adduct of (37).

H_c (Figure 11c) results in enhancements of the signals for the nearby protons H_a, H_m, H_p and H_x. The mutual enhancements observed between H_c and H_x is clearly only consistent with the structure resulting from dienophile attack on the carbonyl-bearing face of the diene. Detailed assignments of the proton and carbon-13 n.m.r. spectra have been interpreted using two-dimensional proton-proton (COSY), proton-carbon (HETCOR) correlation spectroscopy and NOED techniques.

The diene (37) reacted relatively slowly with the electron-deficient mono-substituted alkenes (63-66) and with diethyl maleate (68) to give exclusively the Alder adducts (82-85) resulting from dienophile attack on the carbonyl face of the diene (Scheme 10). In contrast, the electron-rich alkene vinyl acetate (67) and the trans-olefin (69) failed to react over extended reaction times. Similarly, no reaction occurred with the reactive olefin tetracyanoethylene (TCNE) (70).

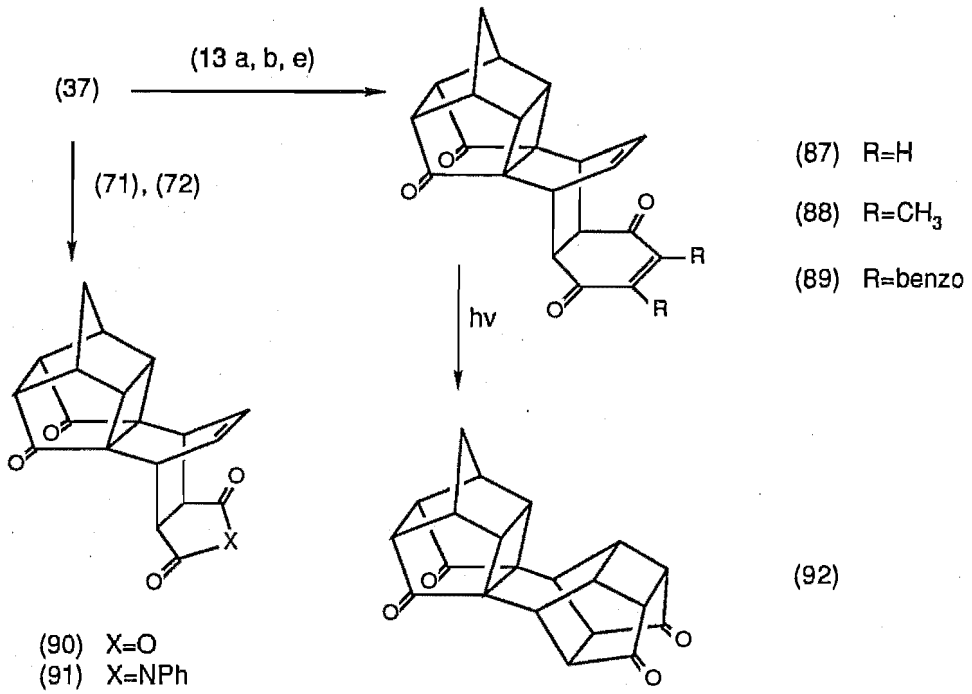
Scheme 10



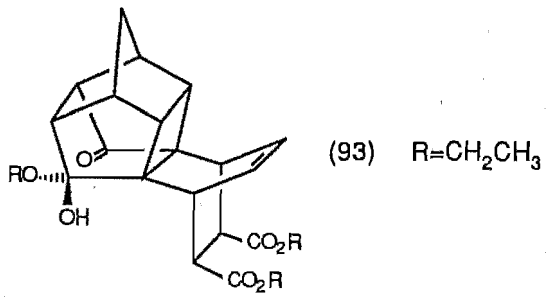
The cyclic dienophiles (13,71,72) reacted more rapidly with (37) with the same stereoselectivity as above to give the adducts (87-91) (Scheme 11). The structure of (87) was shown by X-ray crystallography[101] (described below) to be different from that previously proposed.[97,98] Accordingly the structure of the known[97,98] [$_\pi$2 + $_\pi$2]-photoadduct of (87) is reassigned as (92). Although (87) is readily photolysed in sunlight (3 hr) to the

bis-cage **(92)** the corresponding naphthoquinone adduct **(89)** failed to form a bis-cage product under similar conditions. The

Scheme 11



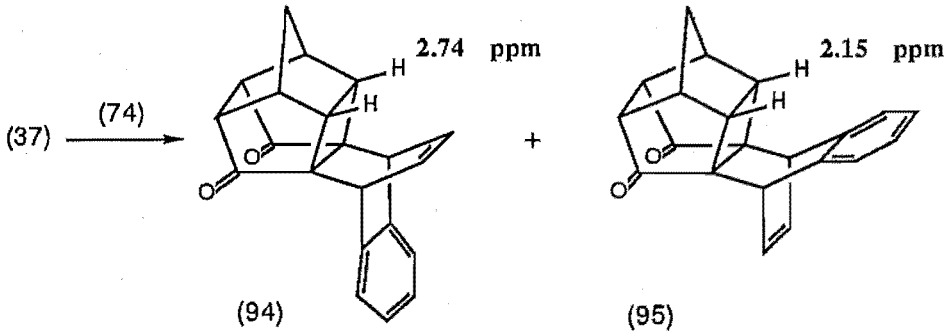
structure of **(90)** was also confirmed by X-ray crystallography[101] (described below) and used to confirm the structure of the diethyl maleate adduct **(86)**, to which it was converted by acid catalysed reaction with ethanol. The mono-hemiacetal **(93)** was also produced in this reaction and unlike the acetal **(62)**, was stable in chloroform solution. Somewhat surprisingly, cyclohex-2-eneone **(73)** failed to react with **(37)**.



(93) R=CH_2CH_3

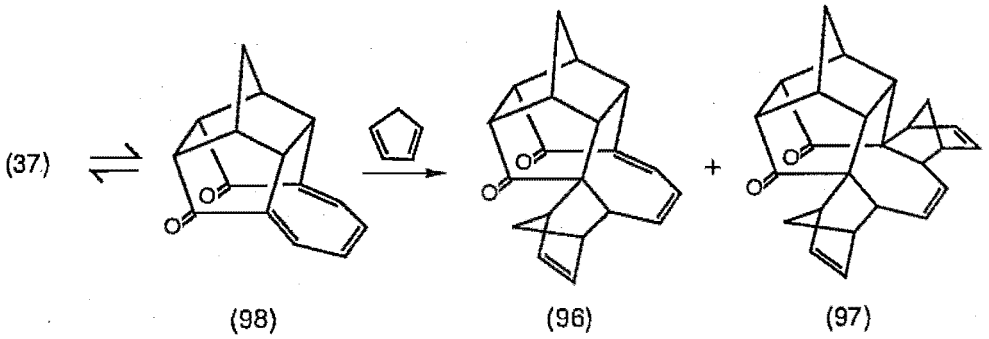
Benzyne (74) reacted with (37) to give a mixture of two adducts, (94) and (95), which were separated by radial chromatography and distinguished, inter alia, by the relatively high field position of the cyclobutane ring protons which lie over the shielding region of the benzene ring in (95) (Scheme 12).

Scheme 12



Reaction of (37) with cyclopentadiene (75) has been previously reported.[99] Reaction with excess cyclopentadiene produced two adducts which were separated by radial chromatography and identified as the known mono-adduct (96) and the new bis-adduct (97) (Scheme 13). The structure of (97) was

Scheme 13



determined by a combination of one- and two-dimensional n.m.r. techniques. The HETCOR spectrum of (97) is shown in Figure 12. These products are formed from Diels-Alder reactions in which cyclopentadiene acts as the diene component and the valence tautomer (98)[99,103] of the diene (37) acts as the dienophile. In

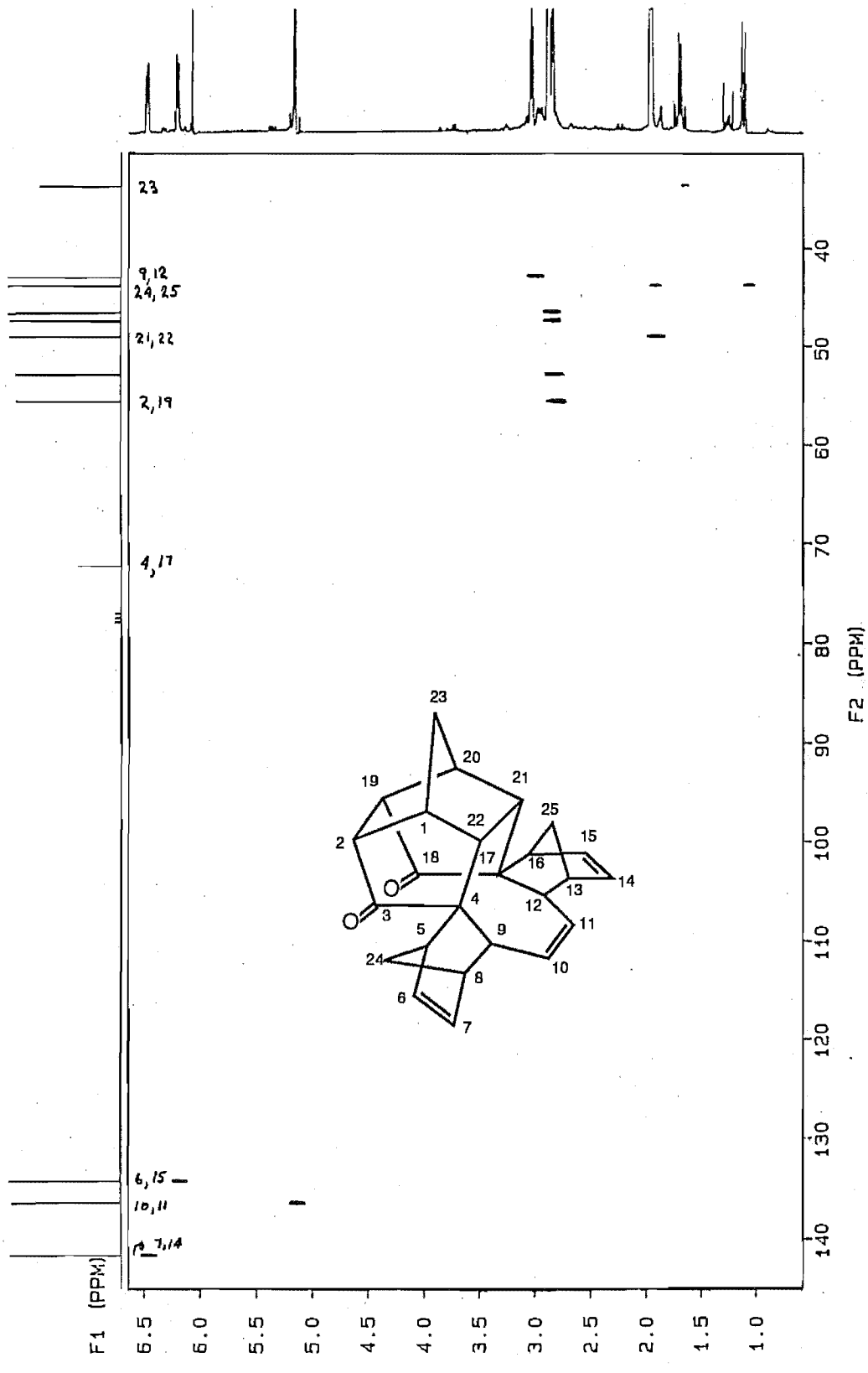
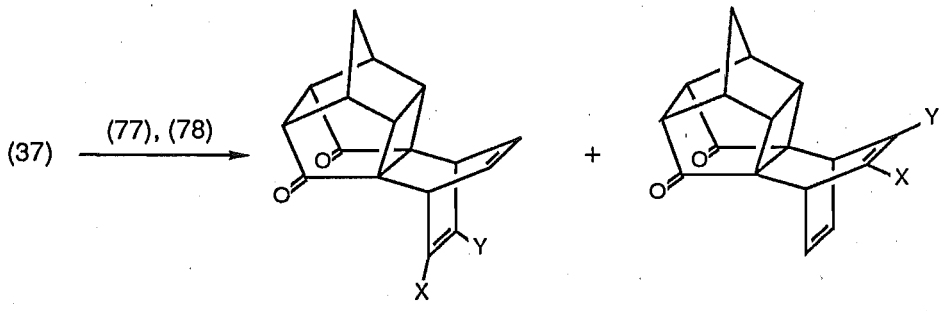


Figure 12. Heteronuclear correlated n.m.r. spectrum of the bis-cyclopentadiene adduct of (37).

contrast, no reaction occurs with indene **(76)** which does not undergo reaction as a diene.

Reaction of **(37)** with the electron-deficient acetylenes **(77)** and **(78)** produced the adducts **(99-101)** (Scheme 14). Thus

Scheme 14



(99) X=H, Y=CO_2Me
(100) X=Y=CO_2Me

(101) X=Y=CO_2Me

methyl propiolate **(77)** reacted stereospecifically to produce a single diastereoisomer resulting from attack on the carbonyl face of the diene, while dimethyl acetylenedicarboxylate (DMAD) **(78)** reacted more rapidly to give a mixture of the two possible isomers. Surprisingly, little change in stereoselectivity occurred when the reaction was carried out at room temperature. The reaction of **(37)** with **(78)** has been twice previously reported[79,99] and in each case only a single product was reported. The structure of **(101)** was determined by X-ray crystallography[101] (described below) and based on the melting points previously reported, Kushner[79] isolated adduct **(100)** whilst Mehta et al[99] isolated the less soluble minor isomer **(101)**. The DMAD adducts could be expected to undergo photolytic rearrangement to give [$_{\pi}2$ + $_{\pi}2$] cycloaddition products but compounds containing bicyclo[2,2,2]octadiene frameworks generally give di-π-methane rearrangement products[104] with sensitised radiation or thermally unstable cycloaddition products[105] with direct irradiation. However, irradiation of samples of **(100)** and

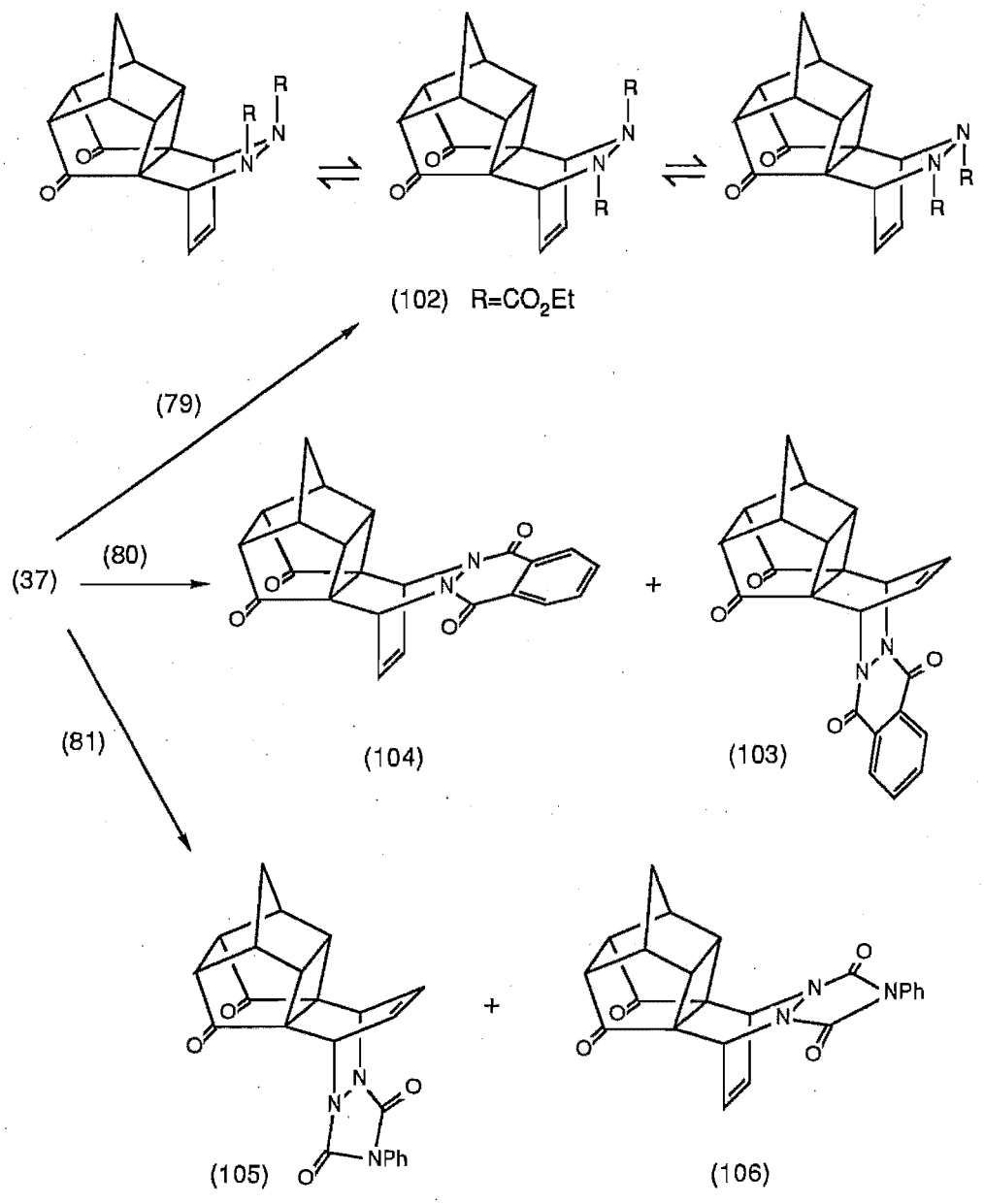
(101) in acetone produced polymeric materials as evident from examination of spectra of crude reaction mixtures.

Diethyl azodicarboxylate (DEAD) (79) reacted with (37) to give a single adduct with an unexpectedly complex n.m.r. spectra. An X-ray crystal structure determination of this product was carried out and is described below. The product was shown to be (102), resulting from attack on the cyclobutane face of the diene. The complexity of the n.m.r. spectra results from slow inversion on the n.m.r. time-scale of the nitrogen atoms, that is slow interconversion of the isomers shown in Scheme 15. Similar dynamic effects on the n.m.r. spectra of related compounds are well known.[106-110]

Phthalazinedione (80) and the very reactive dienophile N-phenyl triazolinedione (PTAD) (81) each reacted with (37) to give a mixture of the two possible diastereoisomers as shown in Scheme 15. In these products however the nitrogen atoms are planar and hence no dynamic n.m.r. effects are observed. In a similar NOED experiment to that conducted for the benzoquinone adduct, an analysis was carried out for a PTAD adduct of unknown stereochemistry. Examination of the NOED spectrum obtained from irradiation of the olefinic protons (δ 6.61 ppm) revealed enhancement of the aliphatic protons at δ 5.04 ppm. However, no enhancement of signals was observed for protons in the region 2.7-3.5 ppm. Successive irradiations of these three sets of protons failed to show an enhancement of the olefinic signal hence these results are consistent with the structure (106) resulting from dienophile attack opposite the carbonyl-bearing face of (37). Also, the low field position of the multiplet at δ 3.42 ppm (H6,H7) confirmed the spacial proximity of these protons to the nitrogen lone pairs.

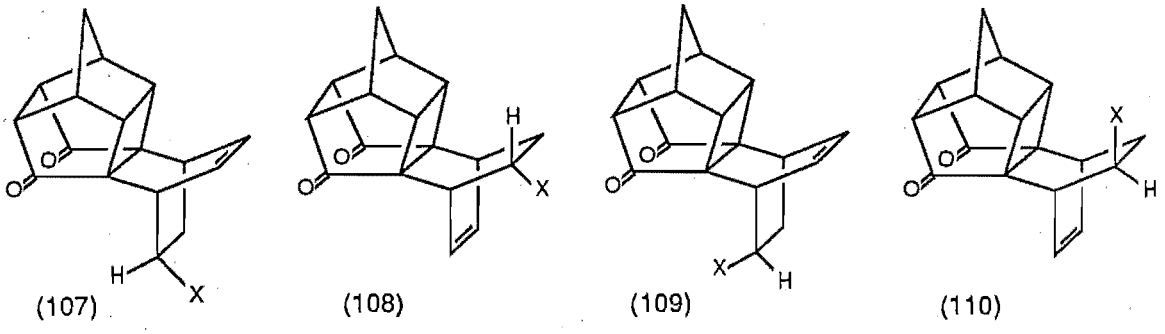
Four isomers, (107-110), are possible products from the Diels-Alder reaction of (37) with a mono-substituted olefin depending on whether attack occurs on the carbonyl face (to produce (107) and/or (109)) or the cyclobutane face (to give (108) and/or (110)) and upon whether the reaction occurs with Alder (107/108) or anti-Alder (109/110) stereoselectivity.

Scheme 15



Although anti-Alder adducts are not uncommon products of Diels-Alder reactions[111] (e.g. reactions of (11)), inspection of molecular models and calculations based on the crystal structure

of (62) (see below) clearly show that the transition states leading to (109) and (110) are strongly destabilized by repulsive (e.g. steric) interactions between the dienophile substituent X and either the carbonyl oxygens or the cyclobutane ring protons.



(107) (108) (109) (110)

Thus none of the products obtained in the Diels-Alder reactions described above are anti-Alder adducts. In many cases the transition states leading to the Alder-adducts are further stabilized by secondary orbital interactions.[9] These observations are also consistent with the fact that only cis-disubstituted olefins react with (37). Thus whereas diethyl maleate (68) reacts smoothly, diethyl fumarate (69) and the normally reactive tetrasubstituted dienophile TCNE (70) both fail to react. On the basis of the above it is probable that (79), which exists principally as the trans-isomer[112], reacts only as the cis-isomer with which it is in equilibrium, thereby explaining the relatively slow reactivity of DEAD compared to other nitrogen dienophiles.

All the olefinic dienophiles studied undergo cycloaddition exclusively from the carbonyl face of the diene component of (37). This selectivity is attributed to an unfavourable steric interaction between the olefinic protons and the cyclobutane ring protons in the transition state for attack from the cyclobutane face. Inspection of molecular models and calculations based on the crystal structures described below suggest that for the

normal Diels-Alder transition state geometry[113] these protons would be required to come unreasonably close to one another. Repulsive steric interactions in the transition state for attack from the carbonyl face are considerably less.

For other dienophiles (benzyne, alkynes and azo compounds), the stereoselectivity is considerably reduced and ranges from exclusive carbonyl face attack (for methyl propiolate) to exclusive cyclobutane face attack (for DEAD). These changes in stereoselectivity can be attributed to a combination of three factors. Firstly, these dienophiles are considerably more reactive and kinetic differentiation between the two facial transition states is expected to be reduced. Secondly, these dienophiles do not possess protons similarly disposed to those in the olefinic dienophiles for interaction with the cyclobutane ring protons as discussed above although azo dienophiles possess lone pairs of electrons on the nitrogen atoms which will interact with these protons. Thirdly, in the transition state for carbonyl face attack the dienophiles all possess π- or non-bonding orbital electron density which will repulsively interact with the electron density of the carbonyl oxygen atoms.

Since π-facial selectivities of Diels-Alder reactions have previously been ascribed to pyramidalization of the diene system[114], an X-ray crystal structure of **(62)** (crystals of **(37)** suitable for crystallography were not available) was carried out in order to determine whether the diene component of this compound is planar. The geometry of the diene moeity of these two compounds is expected to be very similar since the structural differences between the two are remote from the diene component. Figure 13 shows a perspective view with atom labelling of the

structure of **(62)**. Atom coordinates, bond lengths and bond angles are listed in Tables 11-13.

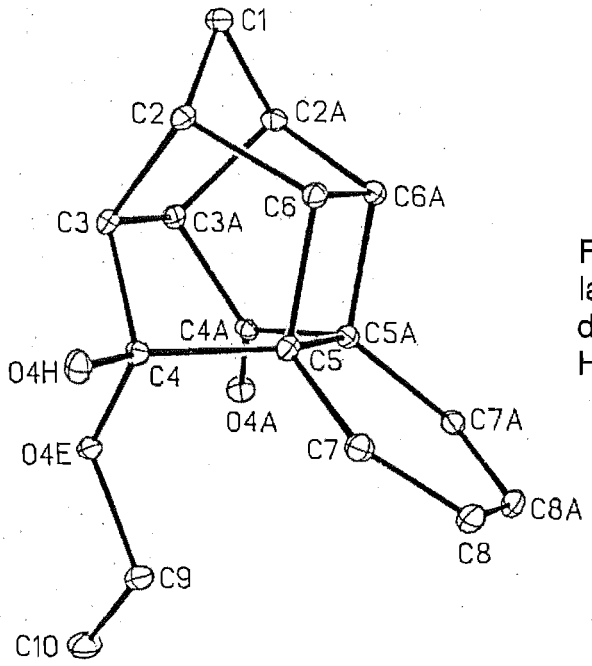


Figure 13. Perspective view and atom labelling of (62). Thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

The structure of **(62)** is thus confirmed as the mono-hemiacetal resulting from ethanol addition to one of the carbonyl groups. Of particular significance is the fact that the ethanol addition has occurred from the "internal" (endo-) face of the carbonyl group. This result is somewhat surprising since reactions involving the carbonyl group of related cage compounds have been assumed[18,22,115,116] to involve nucleophilic attack on the exo-face of the carbonyl group. Although stereospecific exo-reduction of such compounds has recently been unambiguously demonstrated[117], the present result suggests that other reactions (e.g. amine and water additions) may involve attack on the endo-face.

The cyclohexadiene ring is planar (r.m.s. deviation from the meanplane defined by the six carbon atoms: 0.025 (2) Å; all torsional angles about the C-C bonds being $<6^{o}$). Thus there is no significant pyramidalization of the diene carbons in this compound. The bonding geometry in **(62)** is similar to that

previously reported for related cage compounds[52,73,100,101,103] except that the bond elongations of the C3-C3A and C5-C5A bonds are less extreme than those reported for cage diketones in which there is significant electrostatic repulsion between the two carbonyl groups. Another point of interest is that the (non-bonded) O4E-C4A distance (2.612 (2) Å) is considerably longer than that previously[115] estimated (2.20 Å) for this structural unit on the basis of Dreiding models. Similarly the O4E-C4A-O4A angle (100.2 (1)°) is considerably greater than the Dreiding estimate (84°).

Final atom coordinates, bond lengths and bond angles for the four adducts ((87), (90), (101) and (102)) are listed in Tables 14-16. Figures 14-17 show perspective views of the four structures and include the atom labelling. Although compounds (87), (90) and (101) possess molecular symmetry, only the benzoquinone adduct (87) has crystallographic mirror symmetry passing through the C(1) carbon bridge and the mid-point of the double bonds.

The structure of the benzoquinone adduct (87) is that resulting from dienophile attack on the carbonyl-bearing face of the diene and is therefore different from that previously proposed.[97,98] Furthermore, the cycloaddition occurs in an Alder manner, presumably stabilised by secondary orbital interactions.[9] Molecular models show that the anti-Alder transition state is highly destabilised by steric interactions. The structure of (87) (Figure 14) shows that in the ground state the double bonds that interact in this $[_{\pi}2 + _{\pi}2]$ cycloaddition are well separated in space, the C(7)-C(11) interatomic distance being 3.683 (4) Å. The cyclohexenedione ring is planar (to within 0.03 Å) as a result of being fused to a

bicyclo[2,2,2]octane system. This is in contrast to the twisted ring conformation found in benzoquinone Diels-Alder adducts of acyclic dienes.[118]

The structure of the maleic anhydride adduct **(90)** (Figure 15) also corresponds to that resulting from Alder approach on the carbonyl-bearing face of the diene, in agreement with that previously proposed.[78] Comparision of bond lengths and angles (Tables 15 and 16) related by non-crystallographic molecular mirror symmetry shows excellent agreement, mean deviations of related bond lengths and angles being 0.006 Å and 0.7° respectively. As is usual in such adducts[35,119] the five-membered anhydride ring is planar (to within 0.01 Å).

The DMAD adduct **(101)** (Figure 16) results from dienophile attack on the opposite face of the diene. In a previous report[102] this was considered to be the more probable structure. Again bond lengths and angles related by the non-crystallographic mirror symmetry are in excellent agreement (mean deviations 0.005 Å and 0.5° respectively). In this case, however, significant torsional angle differences exist in the relative conformations of the methoxycarbonyl groups (Figure 16), as is commonly the case in dimethyl acetylenedicarboxylate adducts.[118,119]

Because of the complexity of the n.m.r. spectra of the diethyl azodicarboxylate adduct **(102)**, an X-ray crystal structure determination of this compound was carried out in order to determine the stereochemistry of the adduct. Figure 17 shows a perspective view and the atom labelling of **(102)**. The structure is thus shown to be that resulting from dienophile attack on the cyclobutane face of the diene system of **(37)**. Furthermore the two nitrogen atoms are pyramidal with one of the two ethoxycarbonyl substituents in an exo-configuration and the other

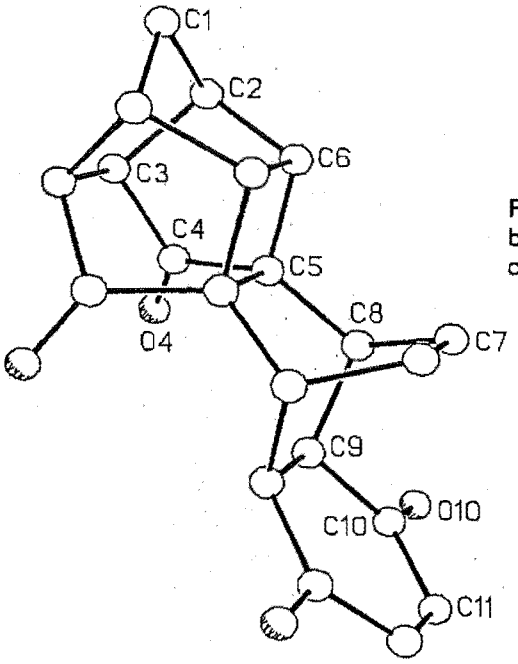


Figure 14. Perspective view and atom labelling of the benzoquinone adduct (87). Hydrogen atoms omitted for clarity.

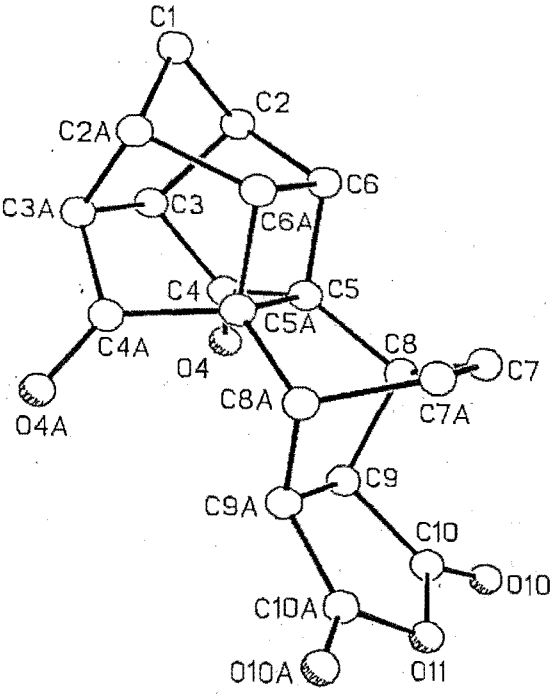


Figure 15. Perspective view and atom labelling of the maleic anhydride adduct (90). Hydrogen atoms omitted for clarity.

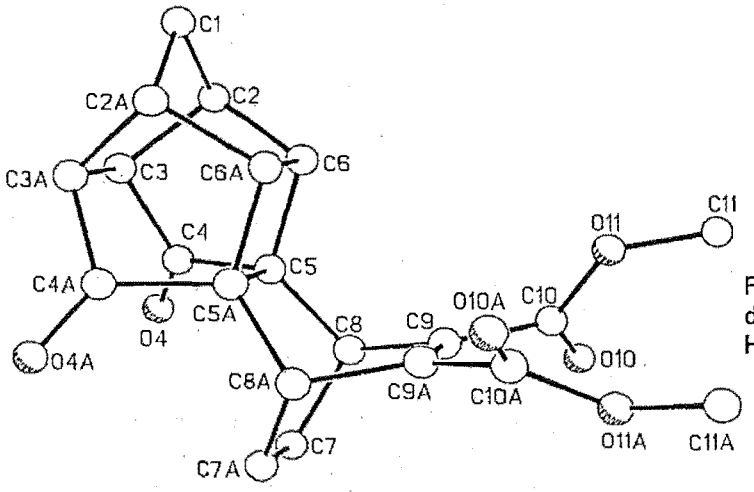


Figure 16. Perspective view and atom labelling of the dimethyl acetylene dicarboxylate adduct (101). Hydrogen atoms omitted for clarity.

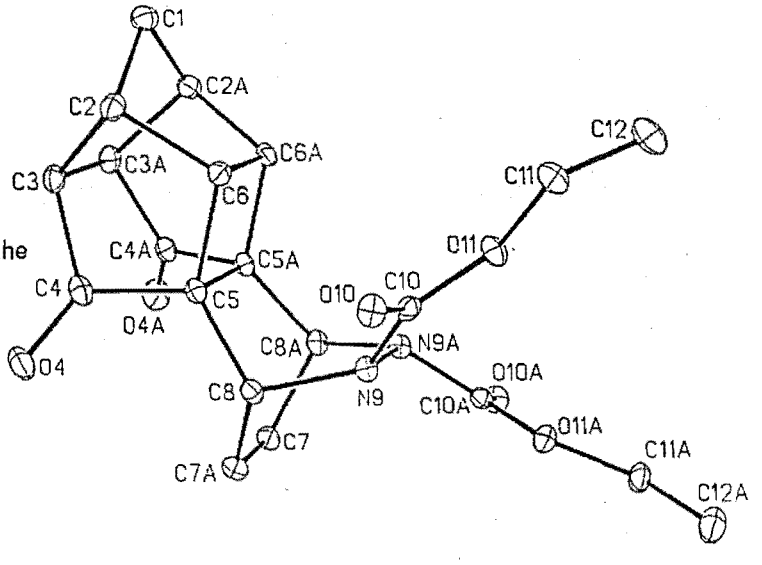


Figure 17. Perspective view and atom labelling of the diethyl azodicarboxylateadduct (102). Thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms omitted for clarity.

endo- with respect to the bicyclo[2,2,2]octane skeleton; this is similar to a related structure which has previously been reported.[120] Other bonding geometry is similar to that in related structures.[52,73,103,120-122]

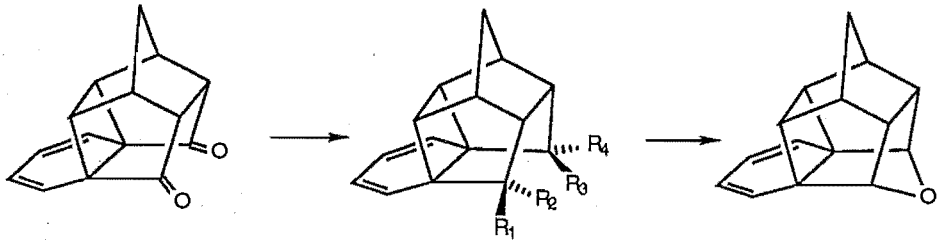
Comparision of equivalent bond lengths and angles among the four structures again shows good agreement, particularly within the 'Cookson-cage' framework.[14] Two notable features in the bonding geometries of all four structures are the significant bond elongations of the C(5)-C(5A) and C(3)-C(3A) bonds (Table 15), the former being a propellane-type bond and both reflecting the mutual repulsion between the C(4) and C(4A) carbonyl groups. Similar effects exist in related structures, which also exhibit similar torsional angles within the cage structure.[52,73,103] Again the geometry of the structures of the four adducts differ from that estimated[115] for a cage diketone using Dreiding models, the distance between the carbonyl carbons and oxygens being 2.606 (3) and 3.988 (2) Å respectively, in contrast to the previously estimated[115] values of 2.44 and 3.52 Å.

The transformation of the diketone (37) to the cyclic ether (112) (Scheme 16) would provide a useful substrate for comparision of the dienophile reaction rates and π-facial selectivities observed for (37).

The diketone (37) was readily reduced with sodium borohydride to give the endo,endo-diol (111a) and endo,exo-diol (111b) in a 3:2 ratio whereas reduction of (37) with sodium borohydride-cerium chloride[117] gave almost exclusively the diol (111a). The external (exo-) proton geminal to the hydroxy group absorbed at an unusually high field (δ 3.58 ppm in (111a) and

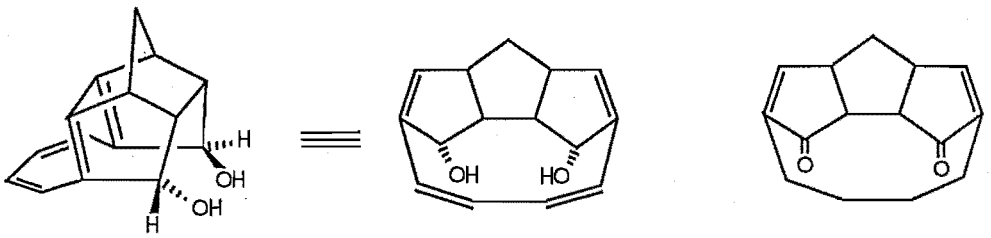
δ 3.68 ppm in (111b)) whereas the internal (endo-) proton in (111b) absorbed in the normal region (δ 4.99 ppm). Attempts at

Scheme 16



(37) (111) a: R_1=R_3=H; R_2=R_4=OH b: R_1=R_4=H; R_2=R_3=OH (112)

dehydrating (111a) with various dehydrating agents (concentrated H_2SO_4[123]; p-toluenesulphonic acid (25°C and 80°C)[117,124]; neat/220°C[115]; neat/P_2O_5[19] and p-toluenesulphonyl chloride[38]) failed. Examination of proton n.m.r. spectra of the crude reaction mixtures indicated polymerisation or recovery of starting material.



(113) (114)

The diol (111a) is highly strained as is evident from the interaction between the internal hydroxy groups at C3 and C10. As a consequence the diol isomerises on silica to the bridged triquinane (113), the structure of which was deduced from spectroscopic methods. That the quaternary propellane carbons (C4,C9) in (111a) were no longer evident and the appearance of two additional olefinic signals in (112) tended to indicate scission of C4-C9 and C13-C14 in (111a). Mehta[125] recently reported the diketone (114) obtained from flash vacuum pyrolysis of the reduced form of (37).

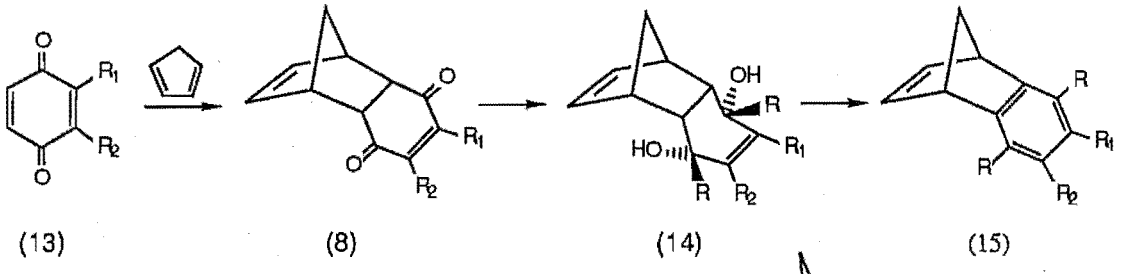
CHAPTER 4

THE CHEMISTRY OF CYCLOPENTADIENE DIELS-ALDER ADDUCTS OF SUBSTITUTED BENZOQUINONES

In this chapter, the synthesis of variously substituted benzo- and naphthonorbornadienes (15) was attempted. The preparation of the diols (14) where R=H was straightforward but addition of organometallic reagents to (8) generally did not provide suitable precursors to hydrocarbons (15).

A series of Diels-Alder adducts (8) were prepared and reduced stereospecifically with sodium borohydride/cerium chloride[117] to the dihydroxy compounds (**14a-e**, R=H). The diol **(14e)** was readily dehydrated with p-toluenesulphonyl chloride/pyridine via the bis-tosylate to give the naphthonorbornadiene **(14e)** as shown in Scheme 3. Attempts to

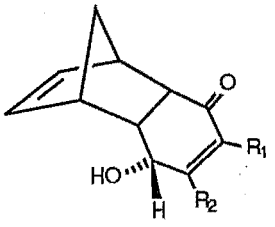
Scheme 3



dehydrate the diols **(14a-d)** by this method and with other dehydrating reagents (potassium bisulphate; phosphoric acid; p-toluenesulphonic acid[126]; p-toluenesulphonic acid/silica[127]; triphenylphosphine/carbon tetrachoride[128] and Martin's sulphurane agent[129]) all failed. Examination of proton n.m.r. spectra of

the crude reaction mixtures showed polymerisation or recovery of starting materials.

The reaction of the adduct **(8d)** with the borohydride /cerium chloride reagent gave in addition to the diol **(14d)** an equal amount of the partially reduced product **(115a)**. It is worth noting that the borohydride reagent attack on the carbonyl group adjacent to the t-butyl group is significantly hindered and that the alternative isomer **(115b)** was not observed.

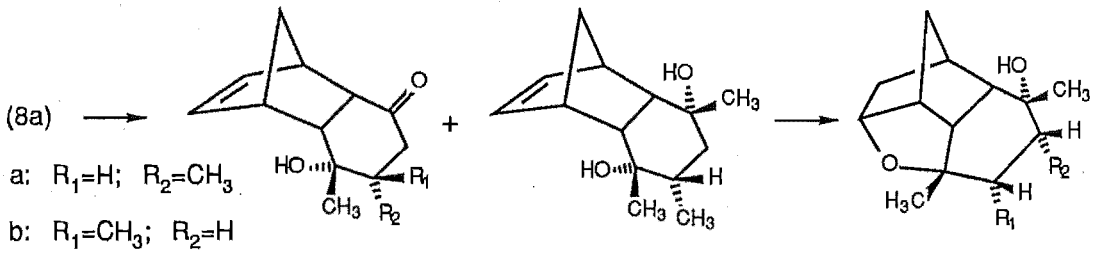


(115) a: R_1=Bu^t; R_2=H
b: R_1=H; R_2=Bu^t

Addition of a five molar excess of organometallic reagents to the adducts **(8a,e)** generally produced undesired 1,4-addition or other by-products, unsuitable for dehydration to ((15), R=Me,Ph), and not the desired 1,2-addition products (14, R=Me,Ph). This is thought to be a consequence of the highly electrophilic nature of the olefinic carbons in the enediones **(8)**.

The benzoquinone adduct **(8a)** reacted with methyl magnesium iodide (Scheme 17) to give two epimeric dimethyl products **(116)** in equal amounts and a trimethyl product **(117)**. In

Scheme 17



(116) 95% (117) 5% (118)

chloroform solution the trimethyl product (117) underwent rearrangement to the cyclised products (118) which were not isolated but readily identified by examination of ^{1}H and ^{13}C n.m.r. Such acid catalysed cyclisations are well established in the literature.[130] The dimethyl products were the result of initial 1,4-addition of a first equivalent of Grignard reagent to either face of the enedione system and subsequent 1,2-addition by a second equivalent of the Grignard reagent, with attack from the methylene bridge face at C6. A recent analysis has shown that the stereochemistry of methyl groups in epimeric compounds could be readily resolved using 1-D NOE methods.[131] The structure and ^{1}H n.m.r. spectral assignments for (116a) were deduced from NOED and homonuclear decoupling experiments as follows; examination of the NOED spectrum obtained from irradiation of the singlet methyl group at C6 (δ 1.33 ppm) revealed enhancements for the protons at δ 2.66 and 3.03 ppm (Figure 18). These protons were easily

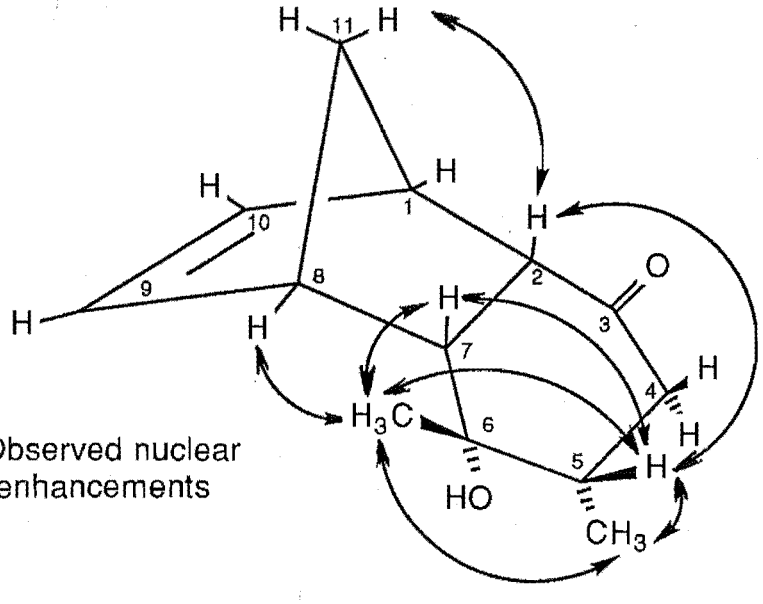


Figure 18. Observed nuclear Overhauser enhancements for (116a).

distinguished and assigned to H7 and H8 respectively. Accordingly, H2 and H1 could be assigned to the four-peak multiplets at δ 2.96 and 3.23 ppm. Homonuclear decoupling methods showed that irradiation of H1 collapsed the multiplet at

δ 6.34 ppm to a doublet and similarly irradiation of H8 collapsed the multiplet at δ 6.18 ppm to a doublet. Accordingly these protons, with a coupling of 5.8 Hz, could be assigned to H10 and H9 respectively. Irradiation of the singlet methyl resonance also produced enhancement of the doublet at δ 0.95 ppm which corresponded to the methyl group at C5. Examination of a Drieding model with the cyclohexanone ring in a skew-boat conformation indicated that the latter methyl group could be in either stereochemistry and still be spacially close to the methyl at C6.

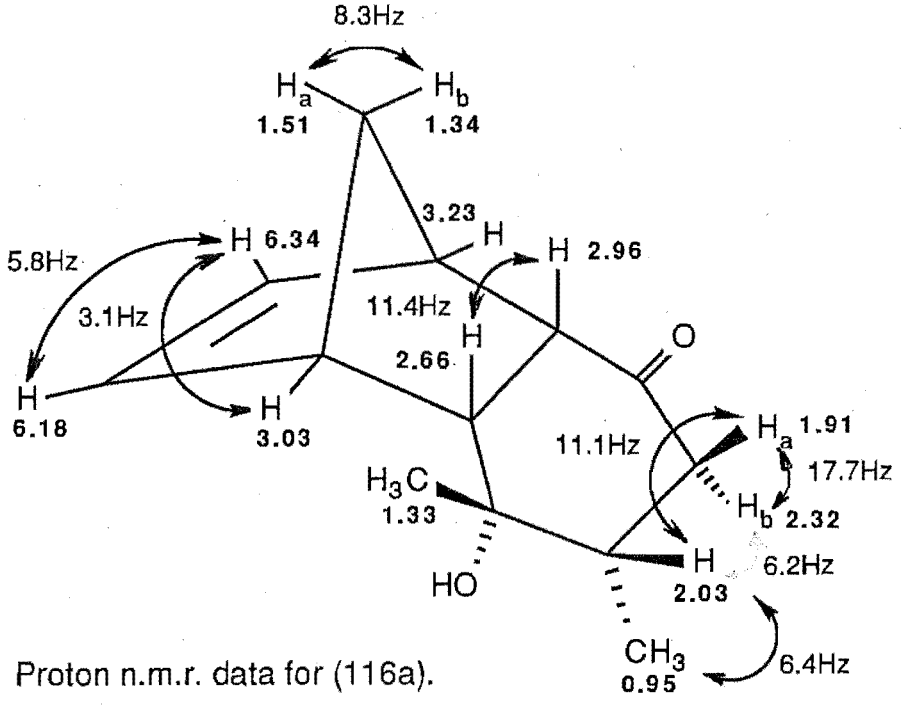


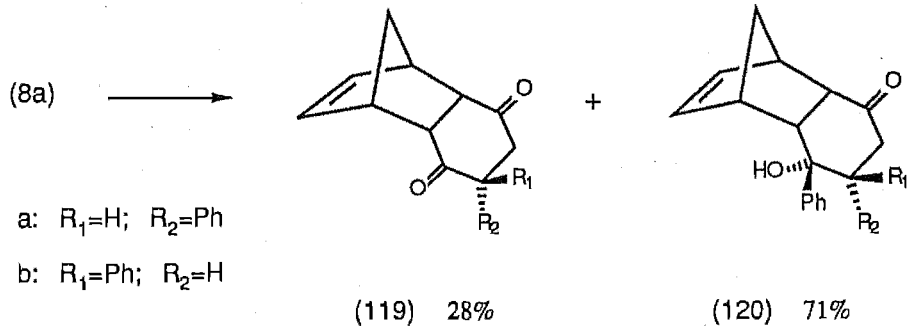
Figure 19. Proton n.m.r. data for (116a).

The relative position of the second methyl group was confirmed by irradiation of the complex multiplet at δ 2.03 ppm accordingly assigned to H5. Enhancements of H2,H7 and the two sets of methyl protons were observed indicating that H5 was on the same face of the molecule as H2 and H7 and hence the methyl group at C5 must be syn to the hydroxy group and anti to the methyl group at C6. The four-peak multiplets at δ 1.91 and 2.32 ppm were assigned to the methylene protons at C5 on the basis of

their large geminal coupling (J 17.7Hz). The former was assigned to H4a on the basis of a larger coupling to H5 (0° dihedral angle) than the latter proton assigned H4b. Finally, irradiation of H2 or H7 showed that the proton at δ 1.34 ppm could be assigned to H11b and hence indirectly the proton at δ 1.51 ppm was assigned to H11a. The observed enhancements for (11**6a**) are shown in Figure 18. With the proton spectrum fully assigned (Figure 19) the assignments of the corresponding ^{13}C n.m.r. signals in (11**6a**) were obtained directly from the HETCOR spectrum. Essentially the same procedure was followed to derive the corresponding spectral assignments for (11**6b**).

The reaction of the benzoquinone adduct (**8a**) with phenyl magnesium bromide (Scheme 18) gave a monophenyl (m.p. 152-153°) and a diphenyl product. Chapman et al[132] reported a monophenyl

Scheme 18



(119) 28% (120) 71%

compound (m.p. 110-111°) obtained by zinc/acetic acid reduction of the cyclopentadiene-phenylbenzoquinone adduct and deduced the stereochemistry of the product to be that where the phenyl group is anti to the methylene bridge (as for (11**9a**)). Only one diphenyl product was observed indicating that there is a favorable orientation of (**8a**) facilitating attack of the first equivalent of Grignard reagent from one face. Comparision of the ^{1}H n.m.r. spectra, and in particular examination of the coupling constants between H5 and H4a/H4b, of the diphenyl product with

those of (116a) and (116b) seems to indicate that the phenyl groups are in an anti-relationship. On this basis (120a) is the most probable structure although (120b) (and hence (119b)) can not be excluded as the reaction products. Examination of a Drieding model suggests an anti-relationship as most likely with 1,2-addition of the second equivalent of phenyl reagent occurring on the methylene-bridge face.

Since (8a) failed to undergo 1,2-addition with Grignard reagents reactions with organolithium reagents were attempted. Methyl lithium was unsuitable as the adduct (8a) enolised to the hydroquinone (121) under these conditions.* It has been reported in the recent literature that combinations of Grignard or alkyl lithium reagents with anhydrous cerium chloride[133] or titanium chloride[134] undergo 1,2-addition smoothly with enolisable ketones. However, these organocerium and organotitanium reagents failed to react with adduct (8a).

The naphthoquinone adduct (8e) reacted with methyl magnesium iodide (Scheme 19) to give four addition adducts that were isolated in addition to a small amount of hydroquinone (122). The proton n.m.r. spectrum of the crude reaction mixture showed other reaction products were present. No products of 1,4-addition were observed presumably a consequence of the resistance of the aromatic ring to nucleophilic attack. Accordingly, two isomeric dimethyl products (123) and a monomethyl product (124) were observed. Of particular interest

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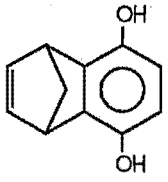
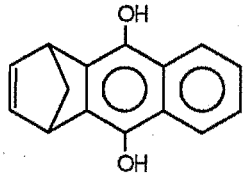
* Since the completion of this work 1,2-addition of methyl lithium to a related substrate has been reported.

See N.H. Buttrus, Sir J. Cornforth, P.B. Hitchcock, A. Kumar and A.S. Stuart, **J. Chem. Soc., Perkin Trans.** 1, 851 (1987).

was the formation of the novel rearrangement product (125) by dehydration of either or both of the diols (123) and a proposed mechanism for this rearrangement is shown in Scheme 20. The



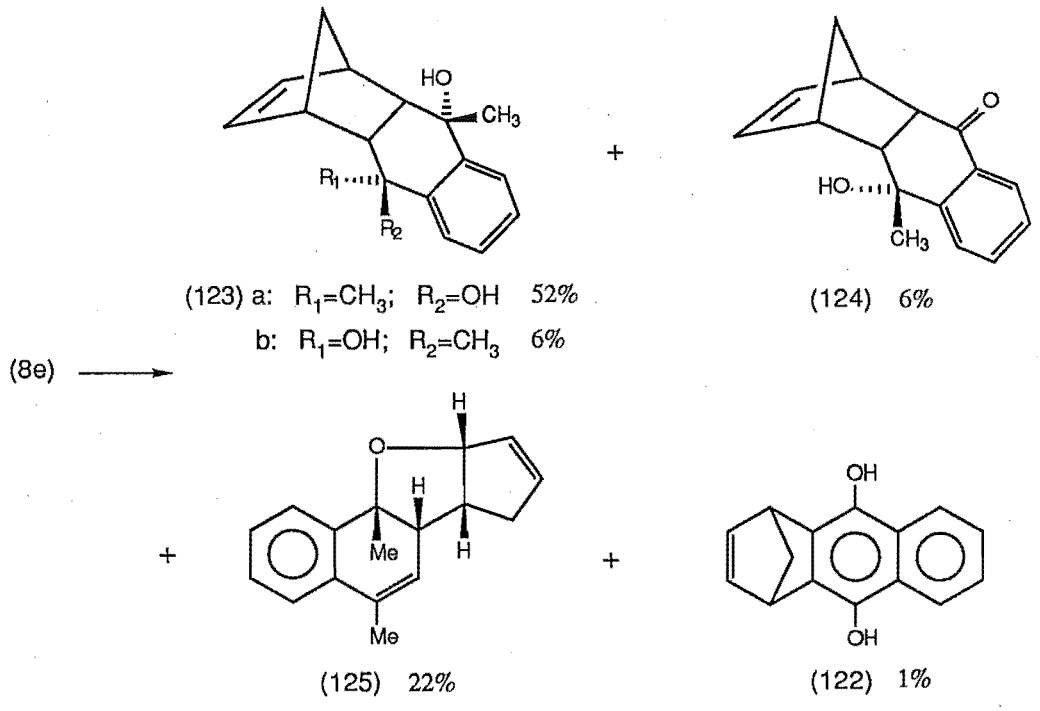
(121)



(122)

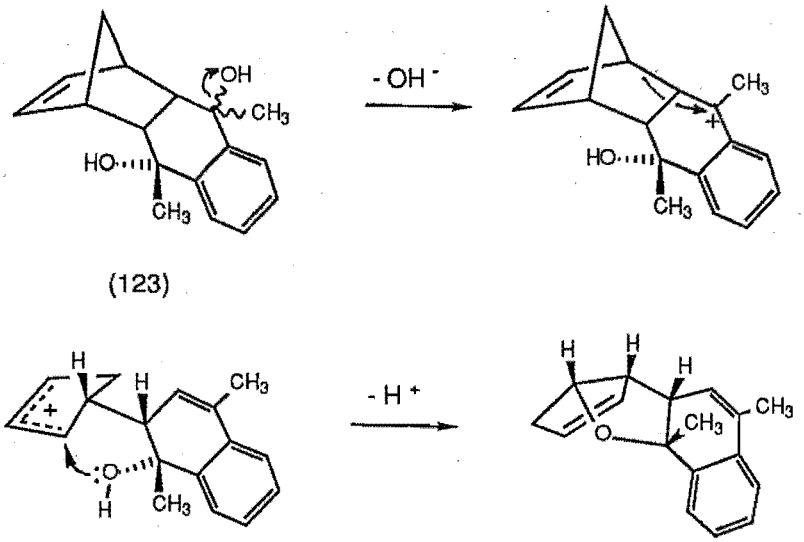
stereochemistry of (123a) was evident from the unsymmetrical nature of the structure. Attempts at recrystallisation of the diol (123a) from ethanol resulted in the formation of two ethoxy derivatives (126) (Scheme 21) of which only one isomer of unknown stereochemistry could be isolated and characterised.

Scheme 19



The structure of (125) was assigned from a combination of spectroscopic methods. Examination of the infra-red spectrum showed the absence of any carbonyl or hydroxyl absorptions and a combination of 2-D n.m.r. and 1-D NOE techniques assisted in the

Scheme 20

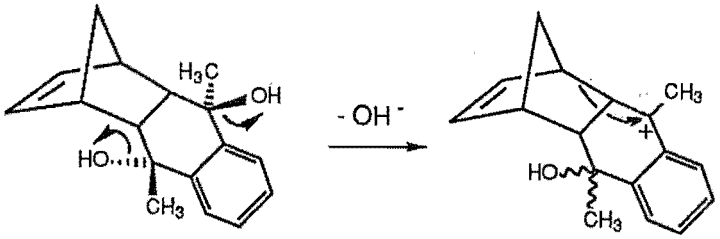


(123)

Intramolecular attack of hydroxy group from underside

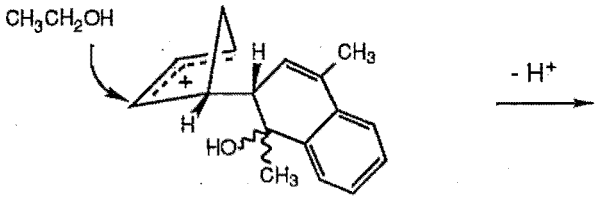
(125)

Scheme 21

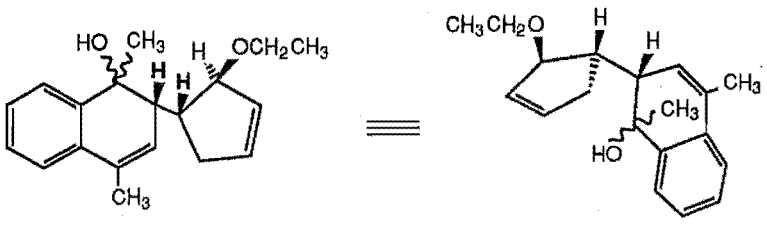


(123a)

Loss of -OH from either face occurs



Attack of allylic cation occurs from top face



(126)

determination of relative stereochemistry. The observed enhancements and proton n.m.r. data for (125) are shown in Figures 20 and 21 respectively. Irradiation of the methine proton, H1, at δ 2.77 ppm produced enhancements for the signals at δ 1.37, 3.07, 5.23 and 5.80 ppm corresponding to the methyl protons at C10 and protons H16, H12 and H2 respectively. This result indicated that (125) was in the orientation as shown in Scheme 20 and the stereochemistry was confirmed by subsequent irradiations of H12, H16 and the methyl group at C10.

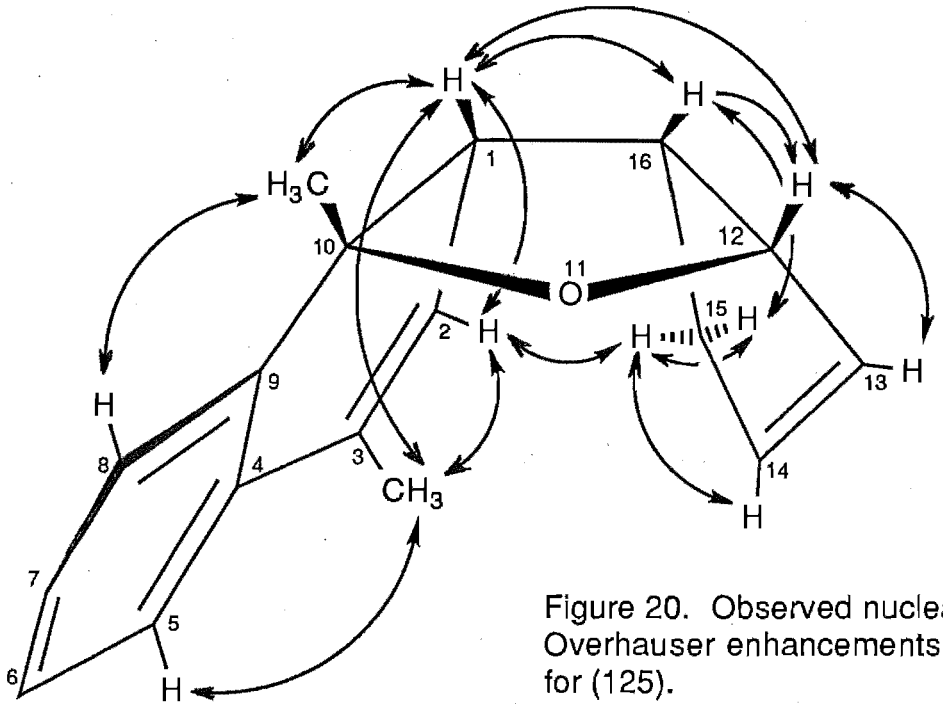


Figure 20. Observed nuclear Overhauser enhancements for (125).

Irradiation of H12 produced enhancement of the multiplet at δ 5.44 ppm allowing the assignment of H13 and indirectly H14 to the multiplet at δ 5.31 ppm. The methylene protons at C15 could be individually assigned from the irradiation of H16 where enhancement of signal occurred for the multiplet at δ 2.02 ppm whereas no enhancement in signal was observed for the multiplet at δ 1.90 ppm. The latter proton was also irradiated and an enhancement was observed for H14, H15a and the proton at δ 5.80 ppm (H2) and hence was assigned H15b and the proton at δ 2.02 ppm

assigned H15a. The aromatic protons absorbed as multiplets at δ 7.15 (3H) and 7.42 (1H) ppm. The latter absorption was assigned to H8 on the basis of a strong NOE to the methyl group at C10. The COSY spectrum assisted in the verification of proton-proton connectivities (Figure 21) and was especially informative in the region of 5.0-6.0 ppm. Assignments

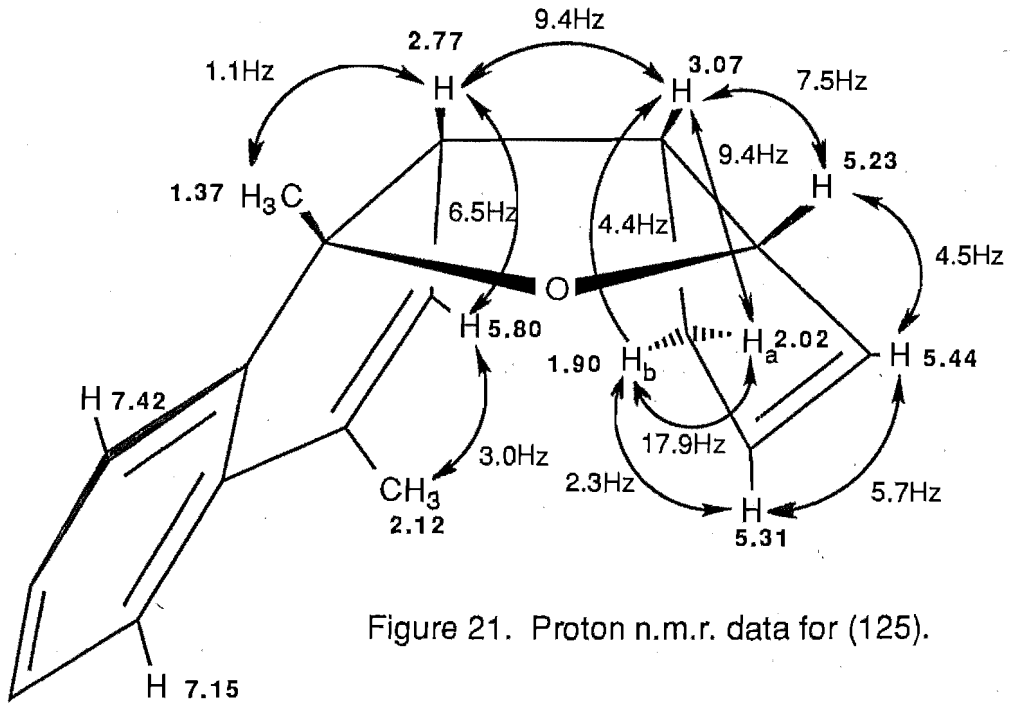


Figure 21. Proton n.m.r. data for (125).

of the corresponding ^{13}C n.m.r. signals in (125), except for the aromatic quaternary carbons, were obtained from the HETCOR spectrum (Figure 22). Demonstrating the usefulness of this technique, the protonated olefinic carbons C2, C13 and C14 could be readily distinguished.

The reaction of the naphthoquinone adduct (8e) with phenyl magnesium bromide (Scheme 22) gave the mono-addition product (127) and the hydroquinone (122) in addition to other products not isolated but evident from inspection of the proton n.m.r. spectrum of the crude reaction product. Integration of the complex aromatic region of the ^{1}H n.m.r. spectrum of (127) revealed that only one equivalent of Grignard reagent had

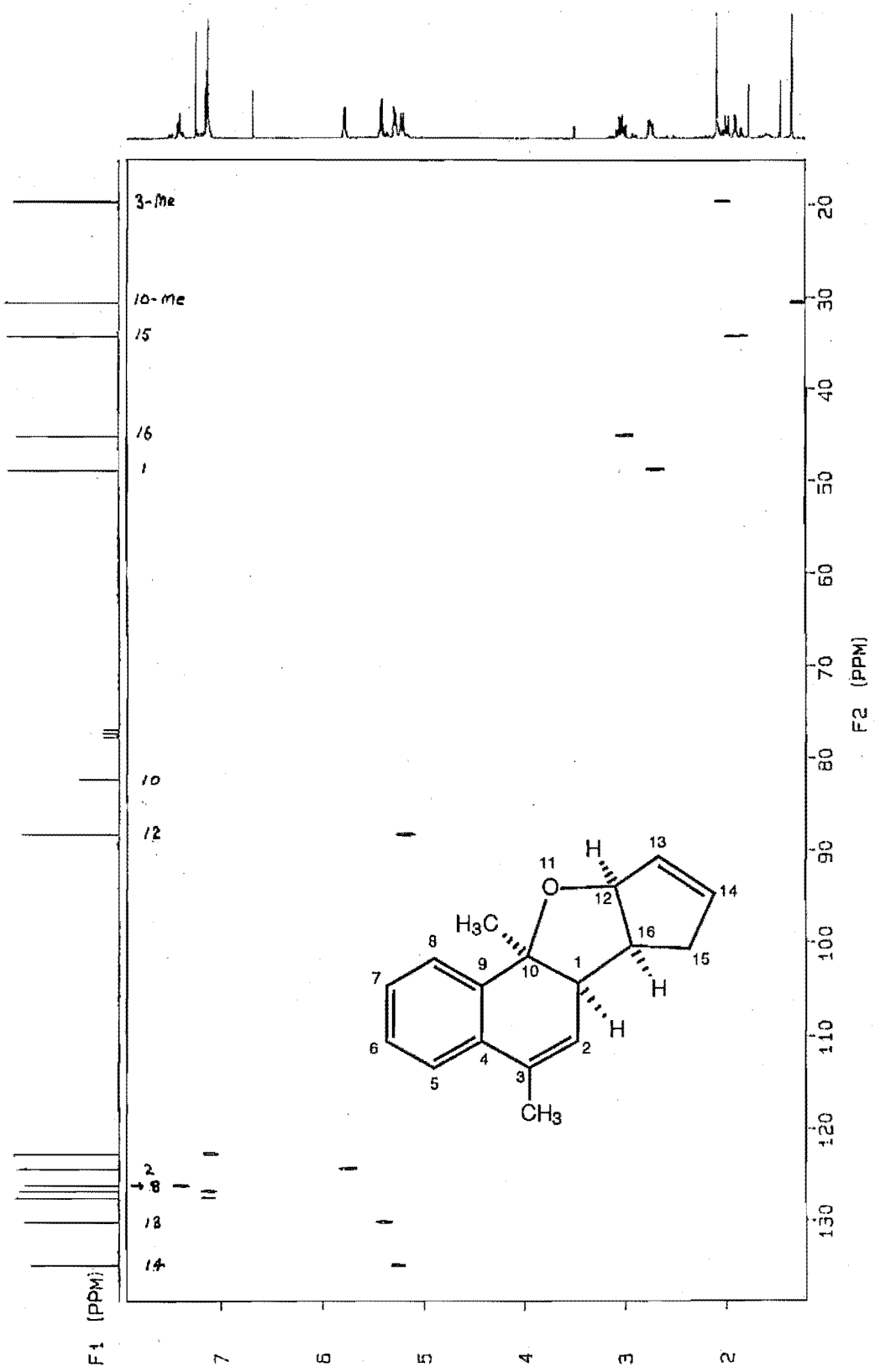
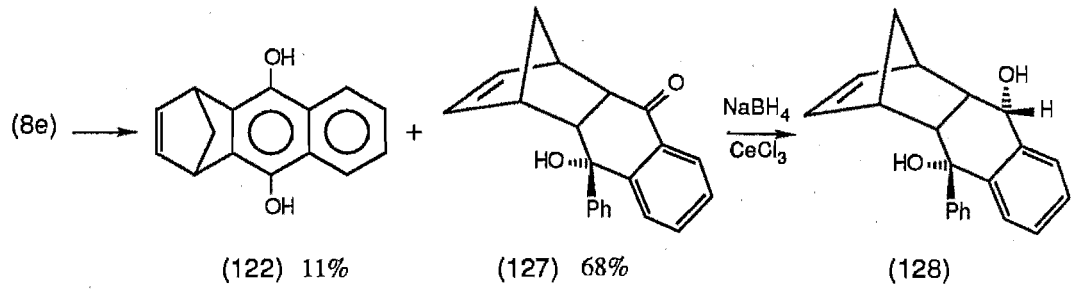


Figure 22. Heteronuclear correlated n.m.r. spectrum of the rearrangement product (125).

reacted with (8e). Reduction of the remaining carbonyl group with sodium borohydride/cerium chloride gave the diol (128).

Scheme 22



(122) 11% (127) 68% (128)

The 1,2-addition of sodium borohydride/cerium chloride to (8a-e) showed the stereospecific nature of this reagent with attack occurring exclusively on the face of the molecule containing the methylene-bridge. Although only the naphthoquinone adduct gave 1,2-addition products with Grignard reagents some interesting chemistry did occur; for example, the formation of the novel rearrangement products (125) and (126) from (123). Future study could involve dehydration of tertiary alcohols (123) and (128), reaction of diols (14) and (123b) with ethanol and the reaction of Grignard reagents with (8b-8d). It is notable that the two Grignard reagents react differently with Diels-Alder adducts (8a) and (8e).

CRYSTALLOGRAPHY

Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatized Mo Kα radiation (λ 0.71069 A). The measured densities were determined by flotation in aqueous potassium iodide or in acidic zinc bromide solutions. Cell parameters were determined by least squares refinement, the setting angles of 25 high angle reflections being used. Throughout data collection the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition except for **(55)** and **(101)** where there was a gradual decrease of 5% in their intensities and which were corrected for by scaling. The intensities were corrected for Lorentz and polarization effects but no corrections were made except in the case of **(23)** where an emperical absorption correction was applied. Significant intensities were recorded for a number of systematically absent reflections for **(55)**, however these were shown to be due to the Renninger effect[135] by azimuthal scan techniques. Reflections with intensities $I > 3\sigma(I)$ were used for structure solution and refinement.

All structures were solved by direct methods and refined by blocked cascade least squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic equivalent of their carrier atoms. In the case of **(22)** the position of the cyclopentenoid double bond was disordered in the two possible positions of the ring with relative population factors of 0.62 and 0.38. The carbon atoms involved in this disorder, C(3)-C(5), refined

successfully as single atoms, whilst the hydrogen atoms were refined with the appropiate site occupancy factors. The two hydroxyl hydrogens in the assymetric unit for **(55)** were included in the positions found from difference maps. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$.

All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL.[136] The scattering factors used were taken from reference 137. Table 17 lists crystal data for the nine structures.

Table 1. Atom coordinates (x 10^4) and temperature factors (Å^2 x 10^3).

Exo isomer - (22)

Atom	10^4x	10^4y	10^4z	10^3U_{eq}
O(1)	7658(2)	5052(2)	2574(1)	55(1)
C(1)	5258(3)	5054(2)	2362(2)	40(1)
C(2)	5546(3)	5129(2)	1153(2)	45(1)
C(3)	5923(3)	6352(3)	619(2)	60(1)
C(4)	7472(3)	5856(3)	-111(2)	72(2)
C(5)	8205(3)	4469(3)	-129(2)	63(1)
C(6)	7096(3)	3875(2)	674(2)	45(1)
C(7)	7620(2)	3216(2)	1646(2)	37(1)
C(8)	6364(2)	2664(2)	2331(2)	37(1)
C(9)	4996(2)	3725(2)	2735(2)	38(1)
C(10)	6991(3)	4536(2)	2276(2)	39(1)
C(11)	4147(3)	6285(2)	3062(2)	43(1)
C(12)	2943(3)	7322(2)	2807(2)	55(1)
C(13)	1934(3)	8420(3)	3494(3)	66(1)
C(14)	2108(3)	8510(3)	4430(2)	71(1)
C(15)	3283(3)	7490(3)	4696(2)	67(1)
C(16)	4285(3)	6389(2)	4021(2)	53(1)
C(21)	3440(3)	3685(2)	3347(2)	42(1)
C(22)	3211(3)	2858(3)	4206(2)	59(1)
C(23)	1762(3)	2761(3)	4705(2)	77(2)
C(24)	518(4)	3505(3)	4379(3)	77(2)
C(25)	710(3)	4345(3)	3549(2)	65(1)
C(26)	2161(3)	4434(2)	3033(2)	52(1)
C(31)	6602(2)	1206(2)	2393(2)	39(1)
C(32)	7876(3)	214(2)	2609(2)	53(1)
C(33)	8047(3)	-1136(2)	2675(2)	67(1)
C(34)	6949(4)	-1519(3)	2551(2)	71(2)
C(35)	5681(3)	-553(3)	2344(2)	68(2)
C(36)	5521(3)	789(2)	2246(2)	53(1)
C(41)	9311(3)	2308(2)	1414(2)	40(1)
C(42)	10150(3)	1484(2)	515(2)	56(1)
C(43)	11680(3)	605(3)	330(2)	70(1)
C(44)	12421(3)	536(3)	1026(2)	68(1)
C(45)	11609(3)	1345(2)	1928(2)	56(1)
C(46)	10077(2)	2213(2)	2115(2)	44(1)

Endo isomer - (23)

Atom	10^4x	10^4y	10^4z	10^3U_{eq}
O(1)	5156(1)	7982(2)	4383(1)	66(1)
C(1)	3917(2)	9699(3)	3740(1)	50(1)
C(2)	3769(2)	11469(3)	3985(1)	58(1)
C(3)	2920(2)	12700(3)	3705(1)	71(1)
C(4)	2016(3)	12971(3)	3940(1)	72(1)
C(5)	2109(2)	12049(3)	4404(1)	63(1)
C(6)	3260(2)	11041(3)	4451(1)	55(1)
C(7)	3169(2)	9054(2)	4450(1)	48(1)
C(8)	2253(2)	8560(2)	3996(1)	45(1)
C(9)	2708(2)	8900(2)	3588(1)	46(1)
C(10)	4263(2)	8714(3)	4226(1)	51(1)
C(11)	4777(2)	9532(3)	3393(1)	58(1)
C(12)	5089(2)	7918(4)	3257(1)	72(1)
C(13)	5890(2)	7687(4)	2951(1)	87(1)
C(14)	6384(2)	9058(5)	2772(1)	95(1)
C(15)	6091(2)	10689(4)	2894(1)	88(1)
C(16)	5287(2)	10921(4)	3208(1)	72(1)
C(21)	2147(2)	8593(3)	3073(1)	47(1)
C(22)	1540(2)	7086(3)	2939(1)	58(1)
C(23)	997(2)	6805(4)	2463(1)	70(1)
C(24)	1039(2)	8002(4)	2107(1)	73(1)
C(25)	1649(2)	9488(3)	2228(1)	70(1)
C(26)	2203(2)	9779(3)	2707(1)	59(1)
C(31)	1027(2)	8101(3)	4015(1)	47(1)
C(32)	708(2)	6853(3)	4319(1)	58(1)
C(33)	-462(2)	6498(4)	4319(1)	77(1)
C(34)	-1329(2)	7363(4)	4016(1)	74(1)
C(35)	-1025(2)	8596(3)	3712(1)	67(1)
C(36)	132(2)	8971(3)	3710(1)	56(1)
C(41)	3110(2)	8181(3)	4927(1)	51(1)
C(42)	3498(2)	6518(3)	5005(1)	62(1)
C(43)	3446(2)	5688(3)	5443(1)	71(1)
C(44)	2999(2)	6501(4)	5803(1)	76(1)
C(45)	2626(3)	8137(4)	5734(1)	81(1)
C(46)	2680(2)	8977(3)	5302(1)	67(1)

U_{eq}, equivalent isotropic U defined as one third of trace of the orthogonalised U_{ij} tensor

Table 2. Bond lengths (Å)

Atoms	(22)	(23)	Atoms	(22)	(23)
O(1)-C(10)	1.200(4)	1.197(2)	C(1)-C(2)	1.565(3)	1.572(3)
C(1)-C(9)	1.542(3)	1.527(3)	C(1)-C(10)	1.540(3)	1.544(3)
C(1)-C(11)	1.510(3)	1.509(3)	C(2)-C(3)	1.532(4)	1.496(3)
C(2)-C(6)	1.567(3)	1.548(3)	C(3)-C(4)	1.416(3)	1.346(4)
C(4)-C(5)	1,376(4)	1.463(3)	C(5)-C(6)	1.521(4)	1.539(3)
C(6)-C(7)	1.580(3)	1.566(3)	C(7)-C(8)	1.537(3)	1.545(2)
C(7)-C(10)	1.536(3)	1.532(3)	C(7)-C(41)	1.500(3)	1.502(3)
C(8)-C(9)	1.354(2)	1.355(3)	C(8)-C(31)	1.486(3)	1.479(3)
C(9)-C(21)	1.474(3)	1.477(2)	C(11)-C(12)	1.390(3)	1.389(4)
C(11)-C(16)	1.384(4)	1.383(4)	C(12)-C(13)	1.392(3)	1.377(4)
C(13)-C(14)	1.367(5)	1.356(5)	C(14)-C(15)	1.371(4)	1.384(5)
C(15)-C(16)	1.384(3)	1.395(4)	C(21)-C(22)	1.386(3)	1.395(3)
C(21)-C(26)	1.388(3)	1.388(3)	C(22)-C(23)	1.384(4)	1.374(3)
C(23)-C(24)	1.370(5)	1.370(4)	C(24)-C(25)	1.363(4)	1.376(4)
C(25)-C(26)	1.385(4)	1.386(3)	C(31)-C(32)	1.392(3)	1.384(3)
C(31)-C(36)	1.389(4)	1.396(3)	C(32)-C(33)	1.387(4)	1.387(3)
C(33)-C(34)	1.368(5)	1.372(3)	C(34)-C(35)	1.372(4)	1.370(4)
C(35)-C(36)	1.381(4)	1.377(3)	C(41)-C(42)	1.390(3)	1.387(3)
C(41)-C(46)	1.390(4)	1.379(3)	C(42)-C(43)	1.378(3)	1.385(3)
C(43)-C(44)	1.371(5)	1.363(4)	C(44)-C(45)	1.384(4)	1.359(4)
C(45)-C(46)	1.376(3)	1.376(4)			

Table 3. Bond angles (degrees)

Atoms	(22)	(23)	Atoms	(22)	(23)
C(2)-C(1)-C(9)	106.7(2)	108.5(2)	C(2)-C(1)-C(10)	96.9(2)	95.7(2)
C(9)-C(1)-C(10)	97.3(2)	96.7(2)	C(2)-C(1)-C(11)	119.9(2)	119.2(2)
C(9)-C(1)-C(11)	115.8(2)	118.0(2)	C(10)-C(1)-C(11)	116.6(2)	114.4(2)
C(1)-C(2)-C(3)	114.6(2)	117.5(2)	C(1)-C(2)-C(6)	104.0(2)	104.7(2)
C(3)-C(2)-C(6)	104.6(2)	105.0(2)	C(2)-C(3)-C(4)	107.6(2)	110.5(2)
C(3)-C(4)-C(5)	113.9(3)	113.8(2)	C(4)-C(5)-C(6)	109.2(2)	104.8(2)
C(2)-C(6)-C(5)	104.6(2)	105.8(2)	C(2)-C(6)-C(7)	104.6(2)	104.6(2)
C(5)-C(6)-C(7)	114.4(2)	117.2(2)	C(6)-C(7)-C(8)	105.4(2)	106.7(1)
C(6)-C(7)-C(10)	97.0(2)	96.6(2)	C(8)-C(7)-C(10)	97.4(1)	97.3(1)
C(6)-C(7)-C(41)	117.0(2)	117.9(2)	C(8)-C(7)-C(41)	118.0(2)	118.0(2)
C(10)-C(7)-C(41)	118.3(2)	116.5(2)	C(7)-C(8)-C(9)	108.6(2)	108.3(2)
C(7)-C(8)-C(31)	124.0(1)	124.0(2)	C(9)-C(8)-C(31)	126.9(2)	126.8(2)
C(1)-C(9)-C(8)	109.0(2)	109.1(2)	C(1)-C(9)-C(21)	123.0(2)	123.9(2)
C(8)-C(9)-C(21)	127.8(2)	127.0(2)	O(1)-C(10)-C(1)	129.9(2)	129.2(2)
O(1)-C(10)-C(7)	130.7(2)	131.6(2)	C(1)-C(10)-C(7)	99.4(2)	99.2(1)
C(1)-C(11)-C(12)	123.1(2)	119.0(2)	C(1)-C(11)-C(16)	119.4(2)	122.8(2)
C(12)-C(11)-C(16)	117.4(2)	118.2(2)	C(11)-C(12)-C(13)	120.6(3)	121.6(3)
C(12)-C(13)-C(14)	120.9(2)	119.7(3)	C(13)-C(14)-C(15)	119.1(2)	120.6(3)
C(14)-C(15)-C(16)	120.4(3)	119.6(3)	C(11)-C(16)-C(15)	121.6(2)	120.4(3)
C(9)-C(21)-C(22)	122.1(2)	120.7(2)	C(9)-C(21)-C(26)	120.0(2)	121.7(2)
C(22)-C(21)-C(26)	117.8(2)	117.6(2)	C(21)-C(22)-C(23)	120.4(3)	121.0(2)
C(22)-C(23)-C(24)	120.8(3)	120.7(2)	C(23)-C(24)-C(25)	119.7(3)	119.4(2)
C(24)-C(25)-C(26)	120.0(3)	120.3(2)	C(21)-C(26)-C(25)	121.3(2)	120.9(2)
C(8)-C(31)-C(32)	122.5(3)	123.9(2)	C(8)-C(31)-C(36)	120.1(2)	118.4(2)
C(32)-C(31)-C(36)	117.4(2)	117.7(2)	C(31)-C(32)-C(33)	120.8(3)	120.7(2)
C(32)-C(33)-C(34)	120.7(3)	120.8(2)	C(33)-C(34)-C(35)	119.2(3)	119.1(2)
C(34)-C(35)-C(36)	120.7(3)	120.7(2)	C(31)-C(36)-C(35)	121.1(2)	121.0(2)
C(7)-C(41)-C(42)	121.3(2)	120.2(2)	C(7)-C(41)-C(46)	121.1(2)	122.3(2)
C(42)-C(41)-C(46)	117.5(2)	117.5(2)	C(41)-C(42)-C(43)	121.1(3)	121.1(2)
C(42)-C(43)-C(44)	120.6(2)	120.0(2)	C(43)-C(44)-C(45)	119.4(2)	119.6(2)
C(44)-C(45)-C(46)	119.9(3)	120.9(3)	C(41)-C(46)-C(45)	121.5(2)	120.9(2)

Table 4. Bond lengths (Å) for (29)

O(2)-C(1)	1.446(2)	O(2)-C(3)	1.467(3)
O(6)-C(6)	1.200(3)	O(10)-C(10)	1.219(2)
C(1)-C(4)	1.590(3)	C(1)-C(8)	1.531(3)
C(1)-C(12)	1.460(3)	C(3)-C(4)	1.578(2)
C(3)-C(7)	1.578(3)	C(3)-C(1')	1.487(2)
C(4)-C(5)	1.577(3)	C(4)-C(1")	1.503(3)
C(5)-C(6)	1.533(3)	C(5)-C(9)	1.572(2)
C(5)-C(5M)	1.512(2)	C(6)-C(7)	1.506(3)
C(7)-C(8)	1.565(3)	C(7)-C(7M)	1.507(3)
C(8)-C(9)	1.530(2)	C(9)-C(10)	1.525(3)
C(10)-C(11)	1.471(4)	C(11)-C(12)	1.335(3)
C(1')-C(2')	1.387(3)	C(1')-C(6')	1.381(3)
C(2')-C(3')	1.387(3)	C(3')-C(4')	1.380(4)
C(4')-C(5')	1.354(5)	C(5')-C(6')	1.377(3)
C(1")-C(2")	1.394(3)	C(1")-C(6")	1.395(2)
C(2")-C(3")	1.395(3)	C(3")-C(4")	1.365(3)
C(4")-C(5")	1.386(3)	C(5")-C(6")	1.376(3)

Table 5. Bond angles (degrees) for (29)

C(1)-O(2)-C(3)	84.6(1)	O(2)-C(1)-C(4)	91.1(1)
O(2)-C(1)-C(8)	106.9(1)	C(4)-C(1)-C(8)	95.2(2)
O(2)-C(1)-C(12)	122.7(2)	C(4)-C(1)-C(12)	121.3(2)
C(8)-C(1)-C(12)	114.5(2)	O(2)-C(3)-C(4)	90.8(1)
O(2)-C(3)-C(7)	104.5(1)	C(4)-C(3)-C(7)	95.5(1)
O(2)-C(3)-C(1')	115.5(2)	C(4)-C(3)-C(1')	127.8(2)
C(7)-C(3)-C(1')	117.5(2)	C(1)-C(4)-C(3)	76.5(1)
C(1)-C(4)-C(5)	105.9(1)	C(3)-C(4)-C(5)	108.4(2)
C(1)-C(4)-C(1")	114.5(2)	C(3)-C(4)-C(1")	121.0(1)
C(5)-C(4)-C(1")	121.2(1)	C(4)-C(5)-C(6)	99.8(1)
C(4)-C(5)-C(9)	101.2(2)	C(6)-C(5)-C(9)	94.8(1)
C(4)-C(5)-C(5M)	123.0(2)	C(6)-C(5)-C(5M)	114.4(2)
C(9)-C(5)-C(5M)	118.6(1)	O(6)-C(6)-C(5)	128.8(2)
O(6)-C(6)-C(7)	130.4(2)	C(5)-C(6)-C(7)	100.8(2)
C(3)-C(7)-C(6)	99.0(1)	C(3)-C(7)-C(8)	96.4(2)
C(6)-C(7)-C(8)	99.8(1)	C(3)-C(7)-C(7M)	118.3(1)
C(6)-C(7)-C(7M)	119.4(2)	C(8)-C(7)-C(7M)	119.3(2)
C(1)-C(8)-C(7)	98.1(1)	C(1)-C(8)-C(9)	99.2(1)
C(7)-C(8)-C(9)	107.6(2)	C(5)-C(9)-C(8)	94.9(1)
C(5)-C(9)-C(10)	113.3(2)	C(8)-C(9)-C(10)	113.4(2)
O(10)-C(10)-C(9)	119.9(2)	O(10)-C(10)-C(11)	121.9(2)
C(9)-C(10)-C(11)	118.3(2)	C(10)-C(11)-C(12)	120.3(2)
C(1)-C(12)-C(11)	115.7(3)	C(3)-C(1')-C(2')	120.1(2)
C(3)-C(1')-C(6')	120.5(2)	C(2')-C(1')-C(6')	119.3(2)
C(1')-C(2')-C(3')	119.6(2)	C(2')-C(3')-C(4')	120.0(3)
C(3')-C(4')-C(5')	120.3(2)	C(4')-C(5')-C(6')	120.5(2)
C(1')-C(6')-C(5')	120.3(2)	C(4)-C(1")-C(2")	122.5(1)
C(4)-C(1")-C(6")	120.0(2)	C(2")-C(1")-C(6")	117.3(2)
C(1")-C(2")-C(3")	120.7(2)	C(2")-C(3")-C(4")	120.7(2)
C(3")-C(4")-C(5")	119.5(2)	C(4")-C(5")-C(6")	120.0(2)
C(1")-C(6")-C(5")	121.8(2)		

Table 6. Atom coordinates (x 10^4) and temperature factors ($Å^2$ x 10^3) for (29).

ATOM	X	Y	Z	U_{eq}*
O(2)	4033(1)	1602(1)	261(2)	46(1)
O(6)	354(1)	1403(1)	-1190(2)	51(1)
O(10)	-866(2)	1536(1)	5097(2)	61(1)
C(1)	2775(2)	1563(2)	1672(2)	39(1)
C(3)	3123(2)	1976(2)	-670(2)	39(1)
C(4)	1988(2)	2675(2)	820(2)	33(1)
C(5)	572(2)	2241(2)	1134(2)	34(1)
C(6)	990(2)	1463(2)	-348(2)	37(1)
C(7)	2377(2)	778(2)	-405(2)	40(1)
C(8)	2085(2)	500(2)	1474(2)	42(1)
C(9)	586(2)	1039(2)	2388(2)	40(1)
C(10)	307(2)	1380(2)	4109(2)	46(1)
C(11)	1481(3)	1521(2)	4522(3)	53(1)
C(12)	2702(2)	1619(2)	3340(3)	51(1)
C(5M)	-746(2)	3167(2)	1430(3)	44(1)
C(7M)	3086(2)	-286(2)	-1519(3)	55(1)
C(1')	3772(2)	2524(2)	-2381(2)	44(1)
C(2')	2989(2)	3378(2)	-3128(3)	54(1)
C(3')	3593(3)	3847(3)	-4744(3)	78(1)
C(4')	4966(4)	3460(3)	-5601(3)	96(2)
C(5')	5727(3)	2622(3)	-4871(3)	95(1)
C(6')	5144(2)	2149(3)	-3266(3)	68(1)
C(1")	2062(2)	4001(2)	1118(2)	34(1)
C(2")	3155(2)	4653(2)	160(3)	42(1)
C(3")	3243(2)	5838(2)	561(3)	48(1)
C(4")	2253(2)	6391(2)	1887(3)	52(1)
C(5")	1161(2)	5759(2)	2858(3)	51(1)
C(6")	1079(2)	4581(2)	2481(2)	43(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 7. Bond lengths (Å) for (55)

O(3)-C(3)	1.204(5)	O(5)-C(4)	1.421(6)
O(5)-C(6)	1.427(5)	O(7)-C(7)	1.207(4)
O(12)-C(12)	1.377(4)	N(1)-C(13)	1.141(6)
C(1)-C(2)	1.554(6)	C(1)-C(11)	1.533(5)
C(1)-C(12)	1.555(5)	C(1)-C(1M)	1.514(5)
C(2)-C(3)	1.509(5)	C(2)-C(8)	1.559(5)
C(3)-C(4)	1.486(6)	C(4)-C(6)	1.468(6)
C(6)-C(7)	1.489(6)	C(7)-C(8)	1.518(5)
C(8)-C(9)	1.556(5)	C(9)-C(10)	1.535(5)
C(9)-C(12)	1.567(5)	C(9)-C(9M)	1.506(5)
C(10)-C(11)	1.337(5)	C(10)-C(1')	1.477(4)
C(11)-C(1")	1.491(5)	C(12)-C(13)	1.487(6)
C(1')-C(2')	1.378(5)	C(1')-C(6')	1.387(5)
C(2')-C(3')	1.386(6)	C(3')-C(4')	1.369(8)
C(4')-C(5')	1.360(7)	C(5')-C(6')	1.382(5)
C(1")-C(2")	1.388(5)	C(1")-C(6")	1.387(6)
C(2")-C(3")	1.380(6)	C(3")-C(4")	1.377(6)
C(4")-C(5")	1.372(5)	C(5")-C(6")	1.382(6)
O(1S)-C(1S)	1.409(6)		

Table 8. Bond angles (degrees) for (55)

C(4)-O(5)-C(6)	62.1(3)	C(2)-C(1)-C(11)	107.2(3)
C(2)-C(1)-C(12)	98.7(3)	C(11)-C(1)-C(12)	99.3(3)
C(2)-C(1)-C(1M)	115.4(3)	C(11)-C(1)-C(1M)	118.7(3)
C(12)-C(1)-C(1M)	114.6(3)	C(1)-C(2)-C(3)	113.9(3)
C(1)-C(2)-C(8)	103.6(3)	C(3)-C(2)-C(8)	115.6(3)
O(3)-C(3)-C(2)	123.9(4)	O(3)-C(3)-C(4)	119.7(3)
C(2)-C(3)-C(4)	116.4(3)	O(5)-C(4)-C(3)	115.2(3)
O(5)-C(4)-C(6)	59.2(3)	C(3)-C(4)-C(6)	118.7(3)
O(5)-C(6)-C(4)	58.8(3)	O(5)-C(6)-C(7)	115.9(3)
C(4)-C(6)-C(7)	117.5(4)	O(7)-C(7)-C(6)	119.6(3)
O(7)-C(7)-C(8)	123.7(3)	C(6)-C(7)-C(8)	116.7(3)
C(2)-C(8)-C(7)	115.6(3)	C(2)-C(8)-C(9)	103.7(3)
C(7)-C(8)-C(9)	114.2(3)	C(8)-C(9)-C(10)	107.9(3)
C(8)-C(9)-C(12)	97.8(2)	C(10)-C(9)-C(12)	99.3(3)
C(8)-C(9)-C(9M)	115.5(3)	C(10)-C(9)-C(9M)	118.0(3)
C(12)-C(9)-C(9M)	115.4(3)	C(9)-C(10)-C(11)	107.9(3)
C(9)-C(10)-C(1')	122.6(3)	C(11)-C(10)-C(1')	129.5(3)
C(1)-C(11)-C(10)	108.4(3)	C(1)-C(11)-C(1")	123.2(3)
C(10)-C(11)-C(1")	128.3(3)	O(12)-C(12)-C(1)	112.2(3)
O(12)-C(12)-C(9)	116.9(3)	C(1)-C(12)-C(9)	94.5(2)
O(12)-C(12)-C(13)	111.4(3)	C(1)-C(12)-C(13)	109.6(3)
C(9)-C(12)-C(13)	111.1(3)	N(1)-C(13)-C(12)	176.6(4)
C(10)-C(1')-C(2')	122.7(3)	C(10)-C(1')-C(6')	119.1(3)
C(2')-C(1')-C(6')	118.1(3)	C(1')-C(2')-C(3')	120.1(4)
C(2')-C(3')-C(4')	121.1(4)	C(3')-C(4')-C(5')	119.4(4)
C(4')-C(5')-C(6')	120.2(5)	C(1')-C(6')-C(5')	121.1(4)
C(11)-C(1")-C(2")	122.1(3)	C(11)-C(1")-C(6")	119.9(3)
C(2")-C(1")-C(6")	118.0(4)	C(1")-C(2")-C(3")	120.6(4)
C(2")-C(3")-C(4")	120.7(3)	C(3")-C(4")-C(5")	119.4(4)
C(4")-C(5")-C(6")	120.2(4)	C(1")-C(6")-C(5")	121.2(3)

Table 9. Atom coordinates (x 10^4) and temperature factors ($Å^2$ x 10^3) for (55).

ATOM	X	Y	Z	U_{eq}*
O(3)	5138(4)	7267(1)	2455(3)	42(1)
O(5)	7116(4)	6947(1)	-273(3)	51(1)
O(7)	3799(4)	6200(1)	-1570(3)	43(1)
O(12)	7420(3)	5828(1)	3523(3)	34(1)
N(1)	4186(5)	5471(1)	4857(4)	50(1)
C(1)	5334(4)	6397(1)	3366(4)	25(1)
C(2)	6176(5)	6573(1)	2175(4)	26(1)
C(3)	5636(5)	7017(1)	1695(4)	33(1)
C(4)	5751(6)	7142(1)	194(4)	46(2)
C(6)	5363(5)	6827(1)	-999(4)	42(2)
C(7)	4836(5)	6400(1)	-632(4)	32(1)
C(8)	5715(4)	6235(1)	917(4)	26(1)
C(9)	4616(4)	5906(1)	1500(4)	24(1)
C(10)	2927(4)	6122(1)	1595(4)	23(1)
C(11)	3351(4)	6407(1)	2688(4)	24(1)
C(12)	5667(4)	5921(1)	3184(4)	27(1)
C(13)	4784(4)	5670(1)	4107(4)	31(1)
C(1M)	6086(5)	6566(1)	4926(4)	33(1)
C(9M)	4474(5)	5479(1)	781(4)	32(1)
C(1')	1192(4)	6004(1)	628(4)	27(1)
C(2')	317(5)	6240(2)	-584(5)	49(2)
C(3')	-1241(5)	6096(2)	-1521(5)	72(2)
C(4')	-1942(5)	5720(2)	-1266(5)	72(2)
C(5')	-1112(5)	5489(2)	-54(6)	58(2)
C(6')	441(5)	5629(1)	894(5)	40(2)
C(1")	2164(4)	6682(1)	3258(4)	26(1)
C(2")	1297(5)	7021(1)	2449(4)	34(1)
C(3")	220(5)	7272(1)	3016(5)	40(2)
C(4")	11(5)	7195(1)	4406(4)	35(1)
C(5")	854(5)	6860(1)	5216(4)	39(1)
C(6")	1915(5)	6605(1)	4646(4)	34(1)
O(1S)	2351(4)	5021(1)	6584(3)	51(1)
C(1S)	1030(5)	5305(1)	6679(5)	55(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 10.

Reaction conditions and Product Ratios for the Diels-Alder reactions of (37).

Dienophile	Reaction Conditions	Products (%) carbonyl face	cyclobutane face
13a	3 hr/80°	**87** (> 98)	(< 2)
13b	24 hr/80°	**88** (> 98)	(< 2)
13e	24 hr/80°	**89** (> 98)	(< 2)
63	4 days/80°	**82** (> 98)	(< 2)
64	5 days/80°	**83** (> 98)	(< 2)
65	7 days/80°	**84** (> 98)	(< 2)
66	8 days/80°	**85** (> 98)	(< 2)
67	6 days/80°	no reaction	
68	9 days/80°	**86** (> 98)	(< 2)
69	9 days/80°	no reaction	
70	5 days/80°	no reaction	
71	24 hr/80°	**90** (> 98)	(< 2)
72	1 hr/80°	**91** (> 98)	(< 2)
73	6 days/80°	no reaction	
74	3 hr/40°	**94** (90)	**95** (10)
76	6 days/80°	no reaction	
77	9 days/80°	**99** (> 98)	(< 2)
78	1 day/80°	**100** (55)	**101** (45)
78	6 days/25°	**100** (60)	**101** (40)
79	5 days/80°	(< 2)	**102** (> 98)
80	5 hr/25°	**103** (43)	**104** (57)
81	15 min/0°	**105** (64)	**106** (51)

Table 11. Atom coordinates (x 10^4) and temperature factors (Å^2 x 10^3) for (62).

atom	x	y	z	U_{eq}
O(4a)	5671(2)	-205(1)	2198(1)	22(1)*
O(4e)	1547(1)	-297(1)	1215(1)	17(1)*
O(4h)	-165(2)	1676(1)	1356(1)	19(1)*
C(1)	5717(2)	4730(2)	1522(2)	20(1)*
C(2)	3535(2)	3980(2)	1560(1)	17(1)*
C(2a)	6459(2)	3616(2)	2108(1)	17(1)*
C(3)	3301(2)	2151(2)	924(1)	15(1)*
C(3a)	5352(2)	1895(2)	1289(1)	16(1)*
C(4)	1648(2)	1391(2)	1601(1)	15(1)*
C(4a)	5138(2)	999(2)	2244(1)	15(1)*
C(5)	2315(2)	2335(2)	2995(1)	16(1)*
C(5a)	4347(2)	2072(2)	3379(1)	16(1)*
C(6)	3365(2)	4054(2)	2950(1)	16(1)*
C(6a)	5379(2)	3807(2)	3334(1)	17(1)*
C(7)	804(2)	2282(2)	3929(1)	19(1)*
C(7a)	4471(2)	1676(2)	4564(1)	20(1)*
C(8)	1164(2)	2035(2)	5015(1)	24(1)*
C(8a)	3002(3)	1668(2)	5325(1)	24(1)*
C(9)	552(2)	-1191(2)	1995(1)	21(1)*
C(10)	779(3)	-2890(2)	1450(2)	29(1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 12. Bond lengths (Å) for (62)

O(4a)-C(4a)	1.209(2)	O(4e)-C(4)	1.425(2)
O(4e)-C(9)	1.440(2)	O(4h)-C(4)	1.396(2)
C(1)-C(2)	1.528(2)	C(1)-C(2a)	1.533(3)
C(2)-C(3)	1.541(2)	C(2)-C(6)	1.545(2)
C(2a)-C(3a)	1.547(2)	C(2a)-C(6a)	1.553(2)
C(3)-C(3a)	1.581(2)	C(3)-C(4)	1.531(2)
C(3a)-C(4a)	1.516(2)	C(4)-C(5)	1.540(2)
C(4a)-C(5a)	1.531(2)	C(5)-C(5a)	1.577(2)
C(5)-C(6)	1.564(2)	C(5)-C(7)	1.495(2)
C(5a)-C(6a)	1.574(2)	C(5a)-C(7a)	1.486(2)
C(6)-C(6a)	1.559(2)	C(7)-C(8)	1.338(3)
C(7a)-C(8a)	1.339(2)	C(8)-C(8a)	1.460(3)
C(9)-C(10)	1.502(2)		

Table 13. Bond angles (degrees) for (62)

C(4)-O(4e)-C(9)	117.1(1)	C(2)-C(1)-C(2a)	95.2(1)
C(1)-C(2)-C(3)	104.5(1)	C(1)-C(2)-C(6)	103.2(1)
C(3)-C(2)-C(6)	100.5(1)	C(1)-C(2a)-C(3a)	104.1(1)
C(1)-C(2a)-C(6a)	103.0(1)	C(3a)-C(2a)-C(6a)	101.3(1)
C(2)-C(3)-C(3a)	103.0(1)	C(2)-C(3)-C(4)	103.2(1)
C(3a)-C(3)-C(4)	111.6(1)	C(2a)-C(3a)-C(3)	102.5(1)
C(2a)-C(3a)-C(4a)	101.4(1)	C(3)-C(3a)-C(4a)	110.7(1)
O(4e)-C(4)-O(4h)	111.1(1)	O(4e)-C(4)-C(3)	106.9(1)
O(4h)-C(4)-C(3)	113.1(1)	O(4e)-C(4)-C(5)	116.1(1)
O(4h)-C(4)-C(5)	107.2(1)	C(3)-C(4)-C(5)	102.3(1)
O(4a)-C(4a)-C(3a)	128.3(1)	O(4a)-C(4a)-C(5a)	126.3(2)
C(3a)-C(4a)-C(5a)	105.0(1)	C(4)-C(5)-C(5a)	111.3(1)
C(4)-C(5)-C(6)	102.6(1)	C(5a)-C(5)-C(6)	90.4(1)
C(4)-C(5)-C(7)	117.5(1)	C(5a)-C(5)-C(7)	115.3(1)
C(6)-C(5)-C(7)	116.0(1)	C(4a)-C(5a)-C(5)	110.8(1)
C(4a)-C(5a)-C(6a)	101.3(1)	C(5)-C(5a)-C(6a)	88.9(1)
C(4a)-C(5a)-C(7a)	115.5(1)	C(5)-C(5a)-C(7a)	116.5(1)
C(6a)-C(5a)-C(7a)	120.2(1)	C(2)-C(6)-C(5)	108.8(1)
C(2)-C(6)-C(6a)	103.3(1)	C(5)-C(6)-C(6a)	90.0(1)
C(2a)-C(6a)-C(5a)	108.4(1)	C(2a)-C(6a)-C(6)	102.9(1)
C(5a)-C(6a)-C(6)	90.7(1)	C(5)-C(7)-C(8)	122.0(2)
C(5a)-C(7a)-C(8a)	121.9(2)	C(7)-C(8)-C(8a)	122.3(2)
C(7a)-C(8a)-C(8)	121.8(2)	O(4e)-C(9)-C(10)	106.8(1)

Table 14.

Atom coordinates (x 10^4) and equivalent isotropic temperature factors (Å x 10^3) for (87).

atom	x	y	z	U^*_{eq}
O(4)	3229(3)	858(2)	4206(2)	26(1)
O(10)	2183(3)	263(2)	8970(3)	46(1)
C(1)†	9070(6)	2500	3631(5)	28(1)
C(2)	7897(4)	1555(2)	4143(3)	23(1)
C(3)	5856(4)	1830(3)	3319(3)	23(1)
C(4)	4664(4)	1410(2)	4482(3)	20(1)
C(5)	5678(4)	1826(2)	6065(3)	20(1)
C(6)	7804(4)	1848(2)	5883(3)	23(1)
C(7)	6398(4)	1944(3)	8954(3)	24(1)
C(8)	5092(4)	1412(2)	7582(3)	21(1)
C(9)	3048(4)	1850(2)	7807(3)	22(1)
C(10)	2316(4)	1279(3)	8945(4)	26(1)
C(11)	1754(4)	1944(3)	10216(4)	30(1)

† Site occupancy = 0.5

Atom coordinates (x 10^4) and equivalent isotropic temperature factors (Å x 10^3) for (90).

atom	x	y	z	U^*_{eq}
O(4)	4489(2)	2868(4)	3738(1)	18(1)
O(4a)	7201(2)	3347(4)	2958(1)	22(1)
O(10)	2111(2)	2050(4)	1177(1)	24(1)
O(10a)	5049(2)	2751(4)	271(1)	32(1)
O(11)	3435(2)	2323(4)	563(1)	18(1)
C(1)	6541(3)	9180(6)	4430(2)	19(1)
C(2)	5498(3)	7837(5)	4258(2)	15(1)
C(2a)	6987(3)	8153(6)	3804(2)	18(1)
C(3)	5924(3)	5561(5)	4307(2)	16(1)
C(3a)	6981(3)	5797(5)	3979(2)	16(1)
C(4)	4981(3)	4457(5)	3703(2)	13(1)
C(4a)	6727(3)	4822(5)	3161(2)	15(1)
C(5)	4716(3)	5858(5)	2977(2)	12(1)
C(5a)	5773(3)	6105(5)	2652(2)	12(1)
C(6)	4948(3)	8091(5)	3345(2)	15(1)
C(6a)	5979(3)	8329(5)	3028(2)	14(1)
C(7)	3537(3)	6970(5)	1649(2)	14(1)
C(7a)	4417(3)	7218(5)	1379(2)	14(1)
C(8)	3683(3)	5305(5)	2283(2)	13(1)
C(8a)	5406(3)	5792(5)	1745(2)	13(1)
C(9)	3977(3)	3198(5)	1937(2)	14(1)
C(9a)	4985(3)	3493(5)	1620(2)	14(1)
C(10)	3054(3)	2490(5)	1228(2)	14(1)
C(10a)	4571(3)	2883(5)	761(2)	19(1)

Atom coordinates (x 10^4) and equivalent isotropic temperature factors (Å x 10^3) for (101).

atom	x	y	z	U^*_{eq}
O(4)	907(1)	6241(2)	-357(1)	29(1)
O(4a)	3892(1)	5164(2)	-944(1)	30(1)
O(10)	1153(1)	2149(2)	2137(1)	32(1)
O(10a)	4755(1)	-540(2)	984(1)	28(1)
O(11)	1771(1)	-847(2)	1608(1)	26(1)
O(11a)	3960(1)	213(2)	1981(1)	28(1)
C(1)	1382(2)	42(3)	-1368(1)	28(1)
C(2)	822(2)	1488(3)	-899(1)	25(1)
C(2a)	2532(2)	779(3)	-1225(1)	25(1)
C(3)	1248(2)	3495(3)	-1131(1)	23(1)
C(3a)	2462(2)	2989(3)	-1363(1)	24(1)
C(4)	1274(2)	4635(3)	-469(1)	21(1)
C(4a)	3246(2)	3865(3)	-651(1)	22(1)
C(5)	1802(2)	3266(3)	35(1)	19(1)
C(5a)	3009(2)	2771(3)	-193(1)	19(1)
C(6)	1434(2)	1211(3)	-208(1)	22(1)
C(6a)	2615(2)	731(3)	-432(1)	21(1)
C(7)	2590(2)	5640(3)	801(1)	24(1)
C(7a)	3607(2)	5217(3)	810(1)	24(1)
C(8)	1817(2)	3925(3)	789(1)	20(1)
C(8a)	3706(2)	3116(3)	417(1)	20(1)
C(9)	2336(2)	2270(3)	1182(1)	20(1)
C(9a)	3365(2)	1865(3)	998(1)	18(1)
C(10)	1696(2)	1291(3)	1724(1)	20(1)
C(10a)	4098(2)	381(3)	1303(1)	21(1)
C(11)	1298(2)	-1753(4)	2240(1)	33(1)
C(11a)	4558(2)	-1352(4)	2302(1)	36(1)

Atom coordinates (x 10^4) and temperature factors (Å x 10^3) for (102).

atom	x	y	z	U^*_{eq}
O(4)	5124(2)	-742(1)	6721(1)	39(1)
O(4a)	2529(2)	1382(1)	5637(1)	38(1)
O(10)	9431(2)	1310(1)	8321(1)	27(1)
O(10a)	7064(2)	3697(1)	5482(1)	31(1)
O(11)	8780(2)	2831(1)	8104(1)	27(1)
O(11a)	9332(2)	3201(1)	6256(1)	27(1)
N(9)	8030(2)	1790(1)	6976(1)	22(1)
N(9a)	7103(2)	2540(1)	6543(1)	22(1)
C(1)	3387(3)	1279(2)	8886(1)	32(1)
C(2)	4478(2)	573(2)	8578(1)	27(1)
C(2a)	3040(2)	1784(2)	7970(1)	28(1)
C(3)	3584(2)	148(1)	7691(1)	26(1)
C(3a)	2563(2)	1006(1)	7265(1)	28(1)
C(4)	4874(2)	-36(1)	7123(1)	25(1)
C(4a)	3172(2)	1350(1)	6422(1)	25(1)
C(5)	5627(2)	837(1)	7205(1)	22(1)
C(5a)	4787(2)	1666(1)	6779(1)	21(1)
C(6)	5670(2)	1203(1)	6189(1)	22(1)
C(6a)	4683(2)	2039(1)	7769(1)	24(1)
C(7)	5920(2)	1462(1)	5365(1)	28(1)
C(7a)	6830(3)	782(2)	5755(1)	31(1)
C(8)	7308(2)	660(1)	6778(1)	24(1)
C(8a)	5591(2)	2187(1)	6076(1)	24(1)
C(10)	8792(2)	1937(1)	7659(1)	22(1)
C(10a)	7801(2)	3179(1)	6030(1)	23(1)
C(11)	9588(3)	3050(2)	9017(1)	30(1)
C(11a)	10080(3)	3976(2)	5853(2)	32(1)
C(12)	9581(3)	4033(2)	9090(2)	42(1)
C(12a)	11765(3)	3902(2)	6182(2)	42(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 15.

Comparision of bond lengths (A)[a]

	(87)	(90)	(101)	(102)
C1-C2	1.518 (4)	1.525 (5)	1.518 (3)	1.522 (3)
C1-C2A		1.523 (5)	1.523 (5)	1.519 (3)
C2-C3	1.546 (4)	1.543 (5)	1.542 (3)	1.543 (3)
C2A-C3A		1.532 (5)	1.542 (3)	1.538 (3)
C2-C6	1.554 (4)	1.559 (4)	1.559 (3)	1.557 (3)
C2A-C6A		1.567 (4)	1.558 (3)	1.559 (3)
C3-C3A	1.596 (6)	1.599 (5)	1.594 (3)	1.594 (3)
C3-C4	1.513 (4)	1.510 (4)	1.516 (3)	1.530 (3)
C3A-C4A		1.515 (5)	1.513 (3)	1.507 (3)
C4-O4	1.210 (3)	1.216 (4)	1.210 (3)	1.207 (3)
C4A-O4A		1.219 (4)	1.206 (3)	1.208 (2)
C4-C5	1.513 (4)	1.513 (4)	1.508 (3)	1.504 (3)
C4A-C5A		1.506 (4)	1.520 (3)	1.515 (3)
C5-C5A	1.606 (6)	1.597 (5)	1.582 (3)	1.594 (3)
C5-C6	1.561 (4)	1.554 (5)	1.554 (3)	1.558 (3)
C5A-C6A		1.553 (5)	1.553 (3)	1.558 (3)
C5-C8	1.526 (4)	1.537 (4)	1.546 (3)	1.529 (3)
C5A-C8A		1.539 (4)	1.547 (3)	1.517 (3)
C6-C6A	1.553 (6)	1.556 (5)	1.548 (3)	1.553 (3)
C7-C7A	1.326 (6)	1.332 (5)	1.324 (3)	1.323 (3)
C7-C8	1.512 (4)	1.512 (4)	1.517 (3)	1.506 (3)
C7A-C8A		1.518 (4)	1.506 (3)	1.513 (3)
C8-C9/N9	1.560 (4)	1.562 (5)	1.512 (3)	1.496 (2)
C8A-C9A/N9A		1.550 (5)	1.517 (3)	1.488 (2)
C9/N9-C9A/N9A	1.550 (6)	1.534 (5)	1.342 (3)	1.429 (2)
C9/N9-C10	1.511 (4)	1.500 (4)	1.482 (3)	1.384 (2)
C9A/N9A-C10A		1.499 (4)	1.483 (3)	1.389 (3)
C10-O10	1.215 (4)	1.191 (4)	1.203 (2)	1.213 (2)
C10A-O10A		1.188 (5)	1.200 (2)	1.210 (2)
C10-O11		1.392 (4)	1.334 (3)	1.331 (2)
C10A-O11A			1.346 (2)	1.336 (2)
C10A-O11		1.408 (4)		
C10-C11	1.465 (4)			
C11-C11A	1.325 (6)			
C11-C12				1.485 (3)
C11A-C12A				1.489 (3)
O11-C11			1.444 (3)	1.455 (2)
O11A-C11A			1.443 (3)	1.462 (2)

[a]N9 and N9A refer to structure (102) only.

Table 16.

Comparision of bond angles (°)[a]

	(87)	(90)[b]		(101)[b]		(102)[b]	
C2-C1-C2A	95.8	95.4		95.2		95.4	
C1-C2-C3	103.8	104.2	104.5	104.5	104.0	109.4	104.5
C1-C2-C6	103.5	103.6	103.1	103.3	103.6	102.8	103.0
C3-C2-C6	101.4	101.2	101.3	101.7	101.5	101.7	101.9
C2-C3-C3A	102.3	102.0	102.6	101.9	102.5	102.2	102.4
C2-C3-C4	103.0	102.0	102.8	102.4	103.8	102.0	103.0
C3A-C3-C4	109.3	110.4	109.9	109.8	108.4	109.8	109.1
C3-C4-C5	104.6	104.6	104.5	104.4	104.2	105.1	104.5
C3-C4-O4	127.6	128.3	127.6	128.1	127.5	128.3	128.9
C5-C4-O4	127.8	127.0	127.8	127.4	128.3	126.6	126.6
C4-C5-C6	103.7	102.8	103.8	103.9	104.4	103.2	104.0
C4-C5-C5A	109.1	111.2	109.2	110.4	108.3	109.2	110.0
C4-C5-C8	120.4	117.4	119.3	116.7	117.5	118.9	115.0
C5A-C5-C6	89.0	89.2	89.3	89.4	89.3	89.1	89.4
C5A-C5-C8	108.9	109.3	109.5	108.9	108.9	107.1	109.4
C6-C5-C8	121.0	123.4	121.5	124.1	124.2	124.9	125.8
C2-C6-C6A	103.0	103.0	102.8	103.2	102.7	103.1	102.8
C2-C6-C5	107.6	107.8	107.2	107.2	107.6	107.7	106.8
C5-C6-C6A	91.0	90.8	90.7	90.5	90.7	90.1	90.9
C7A-C7-C8	114.8	114.5	115.8	114.5	114.6	114.6	113.3
C5-C8-C7	108.0	108.5	108.7	104.4	104.6	106.6	106.9
C5-C8-C9/N9	107.8	105.5	104.8	105.8	106.5	107.5	108.6
C7-C8-C9/N9	107.7	107.8	107.7	108.0	107.6	107.9	107.2
C8-C9/N9-C9A/N9A	109.5	110.5	110.2	114.4	113.9	112.7	111.2
C8-C9/N9-C10	108.3	111.7	113.0	118.9	119.0	116.3	114.1
C9A/N9A-C9/N9-C10	116.8	104.4	105.0	126.7	127.1	118.2	117.7
C9/N9-C10-O10	120.1	129.7	130.7	123.7	123.9	122.4	122.2
C9/N9-C10-C11	120.4						
O10-C10-C11	119.5						
C10-C11-C11A	122.8						
C9/N9-C10-O11		110.6	109.8	112.1	112.3	111.8	113.0
O10-C10-O11		119.7	119.4	124.2	123.8	125.7	124.7
C10-C11-C10A		110.1					
C10-O11-C11				117.1	115.4	115.8	114.5
O11-C11-C12						106.0	107.5
Ave. e.s.d.	0.3	0.2		0.2		0.2	

[a]N9 and N9A refer to structure (102) only.

[b]For (87), (90) and (101) the first value refers to the angle subtended at CX and the second value to that at CXA.

Table 17. Crystal data.

	(22)	(23)	(29)	(55)	(62)	(87)	(90)	(101)	(102)
Formula	$C_{34}H_{26}O$	$C_{34}H_{26}O$	$C_{25}H_{20}O_3$	$C_{26}H_{21}NO_4$	$C_{17}H_{18}O_3$	$C_{21}H_{16}O_4$	$C_{19}H_{14}O_5$	$C_{21}H_{18}O_6$	$C_{21}H_{22}N_2O_6$
Molecular Weight	450.6	450.6	368.4	443.5	270.3	332.4	322.3	366.4	398.4
Crystal System	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/m$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	9.863 (2)	11.610 (1)	10.674 (2)	7.970 (5)	7.011 (1)	7.175 (1)	12.521 (3)	12.257 (4)	8.872 (3)
b (Å)	10.738 (2)	7.862 (2)	10.697 (2)	31.808 (8)	8.977 (2)	11.920 (3)	6.369 (2)	6.858 (2)	14.335 (4)
c (Å)	13.634 (2)	27.675 (3)	8.864 (1)	9.349 (3)	11.216 (2)	8.622 (1)	17.604 (4)	19.610 (5)	14.726 (3)
α (°)	80.90 (1)	90	81.46 (1)	90	108.13 (1)	90	90	90	90
β (°)	68.87 (1)	100.223 (9)	67.47 (1)	106.01 (4)	90.09 (1)	100.18 (1)	107.09 (2)	90.09 (2)	98.75 (2)
γ (°)	66.87 (1)	90	78.92 (1)	90	103.40 (1)	90	90	90	90
V ($Å^3$)	1238	2486	914.3	2278	650.5	725.8	1342	1648	1832
D_c	1.21	1.20	1.34	1.29	1.38	1.52	1.60	1.48	1.44
D_m	1.20	1.17	1.32	——	1.35	1.54	1.59	1.44	1.42
Z	2	4	2	4	2	2	4	4	4
μ (cm^{-1})	0.66	0.66	0.81	0.83	0.87	0.98	1.08	1.01	1.0
F (000)	476	952	388	936	288	348	672	768	840
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
Temperature (°C)	20	20	20	-140	-140	-140	-140	-140	-140
Scan mode	θ/2θ	ω	θ/2θ	ω	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ
2θ range (°)	3-45	3-50	3-48	3-45	3-50	3-50	3-50	3-50	4-50
Unique reflections	3257	4386	2891	2977	2280	1361	2377	2910	3249
Observed reflections	2215	3134	2192	2092	2047	808	1578	2104	2400
Number of parameters	317	316	253	298	184	115	217	244	262
$\|\rho\|$ ($eÅ^{-3}$)	0.19	0.21	0.16	0.27	0.29	0.25	0.42	0.26	0.26
g	0.0007	0.0007	0.00055	0.0018	0.00018	0.0004	0.001	0.0007	0.0006
R (%)	3.9	4.9	3.9	5.9	3.8	4.2	5.2	3.8	4.0
wR (%)	4.8	7.3	5.3	8.0	4.5	4.2	5.5	4.2	5.2

EXPERIMENTAL

Proton and carbon-13 n.m.r. spectra were recorded on Varian T60 and CFT 20 spectrometers respectively (Chapters 1 and 2) or were recorded using a Varian XL-300 spectrometer (Chapters 3 and 4) equipped with a 5 mm probe operating at 299.930 and 75.426 MHz for ^{1}H and ^{13}C respectively. Spectra were recorded on $CDCl_3$ solutions with tetramethylsilane as internal standard, unless otherwise specified. Difference NOE spectra were obtained in an arrayed experiment with the decoupler offset 10,000 Hz and then cycled over the multiplet peaks of the desired proton for irradiation, using a procedure based on that of Kinns and Sanders.[138] COSY spectra were recorded in the normal fashion using the well established pulse sequence and phase cycling of Bax, Freeman and Morris.[139] Heteronuclear proton-carbon correlated spectra were recorded in the usual manner.[140] For several compounds the aromatic carbon signals were coincident and some weak carbon signals were not observed due to limited sample availability.

Infrared spectra were recorded on Shimadzu IR27G or Unicam SP3-300 spectrophotometers as KBr pellets unless otherwise specified. Ultra-violet spectra were recorded in acetonitrile or chloroform solutions on a Varian DMS 100 spectrophotometer. Mass spectra were recorded on A.E.I. MS902 (Chapters 1,2 and 3) or Kratos MS80RFA (Chapter 4) spectrometers. Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck type 60 $P.F._{254}$ silica gel. Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were performed by the Chemistry Department, University of Otago, Dunedin.

The substituted benzoquinones **(13)** were prepared by two-phase oxidation of the corresponding phenols.[141] Unless otherwise stated all dienophiles were obtained commercially.

Diels-Alder reaction of tetracyclone **(5a)** with cyclopentadiene

A solution of tetracyclone (1 g), freshly distilled cyclopentadiene (1 ml) and benzene (5 ml) was heated under reflux for 5 hr until the tetraphenylcyclopentadienone colour was discharged. A proton n.m.r. spectrum of a sample of the crude reaction mixture showed the presence of two isomers in the ratio 4:1. The reaction mixture was cooled, petroleum ether (6 ml) added and the solution cooled to ice temperature. The mixture deposited crystals (0.8 g.) m.p. 188-190° which were recrystallised many times from petroleum ether-dichloromethane to give

endo-1,7,8,9-tetraphenyltricyclo[5,2,1,$0^{2,6}$]deca-3,8-diene-10-one **(23)**, m.p. 195-197° (lit.[55] 197-198°). ν_{max} 1775 cm^{-1} λ_{max} (MeCN) 260.3 nm (ε 6380), 219.5 (17640). ^1H n.m.r. δ_H 2.77, $W_{h/2}$ 10Hz, $(H5)_2$; 3.55, $W_{h/2}$ 20Hz, H6; 4.22, $J_{2,6}$ 10Hz, H2; 6.08 $W_{h/2}$ 3Hz H3,H4; 6.74, $W_{h/2}$ 16Hz, 7.35, $W_{h/2}$ 8Hz, phenyls. ^{13}C n.m.r. δ_C 36.5, C5; 42.1, C6; 52.6, C2; 65.6, 66.0 (C1,C7); 136.0, 136.4 (C3, C4); 140.9, 142.6 (C8,C9), 201.4, C10 (Found: $M^{+\cdot}$, 450.1982; $C_{34}H_{26}O$ requires: $M^{+\cdot}$ 450.1984). The residue from the mother liquor of the first crystallisation was recrystallised several times from methanol to give

exo-1,7,8,9-tetraphenyltricyclo[5,2,1,$0^{2,6}$]deca-3,8-diene-10-one[46] **(22)** (0.1 g.), m.p. 150-152°. ν_{max} 1780 cm^{-1}. λ_{max} (MeCN) 260 nm (ε 10810), 221 (32760). ^1H n.m.r. δ_H 2.32, 2.63, $J_{5,6}$ 2.5Hz, ^2J 18Hz, $(H5)_2$; 3.63, $J_{6,5}$ 2.5Hz, $J_{6,2}$ 9Hz, H6; 4.0, $J_{2,6}$ 9Hz, H2; 5.67, $W_{h/2}$ 2Hz, H3,H4; 6.76, $W_{h/2}$ 12Hz, 7.37,

$W_{h/2}$ 14Hz, phenyls. ^{13}C n.m.r. δ_C 35.6, C5; 44.7, C6; 56.5, C2; 65.2, 66.0, (C1,C7); 134.3, 134.4, (C3,C4); 144.9, 144.6, (C8,C9); 202.1, C10 (Found: $M^{+\cdot}$ 450.1986. $C_{34}H_{26}O$ requires: $M^{+\cdot}$ 450.1984).

Hydrogenation reactions of dienes (22) and (23)

A mixture of **(23)** (210 mg) in ethanol-benzene (100 ml; 1:9) and Adams catalyst ($PtO_2.H_2O$) (25 mg) was agitated in a hydrogen atmosphere (2 atm) for 18 hr. The catalyst was removed and after removal of solvent the residue was recrystallised from petroleum ether to give endo-1,7,8,9-tetraphenyltricyclo[5,2,1,$0^{2,6}$]dec-8-ene-10-one, **(26)** (110 mg), m.p. 212.5-213.5° (lit.[55] 209-211°). ν_{max} 1770 cm^{-1}. λ_{max} (MeCN) 267 nm (ε 7100), 223 (19480). ^1H n.m.r. δ_H 1.45-2.77, $(CH_2)_3$; 3.30, $W_{h/2}$ 10Hz, H2,H6; 6.80, $W_{h/2}$ 18Hz, 7.42, $W_{h/2}$ 6Hz, phenyls. ^{13}C n.m.r. δ_C 27.8, C4; 30.6, C3,C5; 46.5, C2,C6; 66.5, C1,C7; 142.39, C8,C9; n.o., C10 (Found: $M^{+\cdot}$, 452.2134. $C_{34}H_{28}O$ requires: $M^{+\cdot}$ 452.2140).

A mixture of **(22)** (83 mg) and Adams catalyst (20 mg) in ethanol-benzene (100 ml; 1:9) was hydrogenated as above to give exo-1,7,8,9-tetraphenyltricyclo[5,2,1,$0^{2,6}$]dec-8-ene-10-one[46] **(25)** which was precipitated recrystallised from methanol-dichloromethane as an amorphous powder (45 mg), m.p. 157.5-158.5°. ν_{max} 1775 cm^{-1}. λ_{max} (MeCN) 256 nm (ε 9180), 217 (27000). ^1H n.m.r. δ_H 1.0-2.3, $(CH_2)_3$; 3.33, $W_{h/2}$ 14Hz, H2,H6; 6.77, $W_{h/2}$ 18Hz, 7.35, $W_{h/2}$ 18Hz, phenyls. ^{13}C n.m.r. δ_C 30.2, C4; 30.4, C3,C5; 48.46, C2,C6; 64.9, C1,C7; 145.35, C8,C9; n.o., C10 (Found: $M^{+\cdot}$ - CO, 424.2206. $C_{34}H_{28}O$ requires: $M^{+\cdot}$ - CO, 424.2191).

Diels-Alder reactions of hemicyclone (5b)

General procedure: Equimolar quantities (15 mmoles) of hemicyclone[142] and a benzoquinone (13a-e) were dissolved in benzene (15 ml) and heated under reflux for 90 min to 48 hr. For p-benzoquinones (13a-c,e) the adduct precipitated from the reaction mixture. In each case the mother liquors were examined and found to contain starting reagents. For benzoquinone (13d) the adducts did not precipitate and the exo- and endo-isomers were separated by chromatography on silica. For reaction of hemicyclone with cyclohex-2-eneone the mixture was heated under reflux for 48 hr, filtered to remove insoluble materials and after removal of solvent the exo- and endo- adducts were separated by fractional crystallisation.

i) Reaction of hemicyclone with benzoquinone (13a) gave endo-1,8-dimethyl-9,10-diphenyltricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene-3,6,11-trione (20) (5.4 g) which was recrystallised from benzene-chloroform as pale yellow prisms, m.p. 195-197° (lit.[48] 220°). ν_{max} 1760, 1670 cm^{-1}. λ_{max} (MeCN) 263nm (ε 6400), 225 (20600). ^{1}H n.m.r. δ_H 1.55, methyl protons; 3.28, H2,H7; 6.85, H4,H5; 6.6-7.3, phenyls. ^{13}C n.m.r. δ_C 11.8, 1-Me, 8-Me; 51.9, C2,C7; 58.9, C1,C8; 127.7, 128.3, 129.4, phenyl carbons; 133.2, ipso phenyl carbons; 141.6, C9,C10; 143.8, C4,C5; 195.6, C3,C6; 199.7, C11 (Found: $M^{+}\cdot$, 368.1410. $C_{25}H_{20}O_3$ requires: $M^{+}\cdot$, 368.1412).

ii) Reaction of hemicyclone with 2,3-dimethylbenzoquinone (13b) gave endo-1,4,5,8-tetramethyl-9,10-diphenyltricyclo[6,2,1,$0^{2,7}$]undeca-

4,9-diene-3,6,11-trione **(31b)** (3.5 g) which was recrystallised from benzene-chloroform as pale yellow prisms, m.p. 200-202°. ν_{max} 1775, 1660 cm^{-1}. λ_{max} (MeCN) 251nm (ε 21200), 229 (20400). ^1H n.m.r. δ_H 1.53, 1-Me, 8-Me; 1.97, 4-Me, 5-Me; 3.30, H2,H7; 6.6-6.9 (4H), 6.9-7.3, (6H), phenyls. ^{13}C n.m.r. δ_C 11.9, 1-Me, 8-Me; 13.8, 4-Me, 5-Me; 51.6, C2,C7; 59.3, C1,C8; 127.6, 128.2, 129.6 phenyl carbons; 133.3, ipso phenyl carbons; 141.3, C9,C10; 149.9, C4,C5; 194.9, C3,C6; 200.2, C11 (Found: $M^{+\cdot}$, 396.1719; C, 81.7; H, 5.9. $C_{27}H_{24}O_3$ requires: $M^{+\cdot}$, 396.1725; C, 81.8; H, 6.1%).

iii) Reaction of hemicyclone with 2-methylbenzoquinone **(13c)** gave endo-1,4,8-trimethyl-9,10-diphenyltricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene-3,6,11-trione **(31c)** (4.0 g) which was recrystallised from hexane-dichloromethane as yellow prisms, m.p. 177-179°. ν_{max} 1780, 1670 cm^{-1}. λ_{max} (MeCN) 273sh (ε 6500), 228 (24300) nm. ^1H n.m.r. δ_H 1.52, 1.57 (1-Me,8-Me); 1.95, $W_{H/2}$ 4Hz, 4-Me; 3.28, H2,H7; 6.6-7.0 (5H), phenyls, H5; 7.0-7.3 (6H), phenyls. ^{13}C n.m.r. δ_C 11.7, 12.0, (1-Me,8-Me); 17.1, 4-Me; 51.8, 52.5, (C2,C7); 59.1, C1,C8; 127.7, 128.2, 129.5, phenyl carbons; 133.3, ipso phenyl carbons; 141.2, C9,C10; 141.8, C5; 153.7, C4; 195.4, 195.8 (C3,C6); 200.0, C11. (Found: $M^{+\cdot}$, 382.1569; C, 81.8; H, 6.2. $C_{26}H_{22}O_3$ requires: $M^{+\cdot}$, 382.1569; C, 81.7; H, 5.8%).

iv) Reaction of hemicyclone with 2-tert-butylbenzoquinone **(13d)** gave a residue which was absorbed onto silica on radial chromatograph. Elution with ether-petroleum ether (1:9) gave endo-4-tert-butyl-1,8-dimethyl-

9,10-diphenyltricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene-3,6,11-trione **(31d)** (0.2 g) which was recrystallised from hexane-dichloromethane as yellow prisms, m.p. 150-152°. ν_{max} 1775, 1665 cm^{-1}. λ_{max} (MeCN) 275sh (ε 5600), 231 nm (22100). ^1H n.m.r. δ_H 1.15, Bu^t; 1.55, 1.67 (1-Me,8-Me); 3.28, H2,H7; 6.77, H5; 6.7-7.3, phenyls. ^{13}C n.m.r. δ_C 12.2, 12.6 (1-Me,8-Me); 29.1 t-Bu; 35.9, C_q(Bu); 51.8, 53.2, (C2,C7); 58.8, 59.0, (C1,C8); 127.6, 127.9, 128.2, 129.6, 130.2, phenyl carbons; 133.2, 133.7, ipso phenyl carbons; 139.8, C5; 141.8, 142.3, (C9,C10); 163.5, C4; 195.3, 196.9, (C3,C6); 200.3, C11 (Found: C, 82.1; H, 6.8. $C_{29}H_{28}O_3$ requires: C, 82.1; H, 6.7%). Further elution gave exo-4-tert-butyl-1,8-dimethyl-9,10-diphenyl-tricyclo[6,2,1,$0^{2,7}$]-undeca-4,9-diene-3,6,11-trione **(32d)** (0.2 g) which was recrystallised from hexane-dichloromethane as pale yellow prisms, m.p. 157-159°. ν_{max} 1775, 1665 cm^{-1}. λ_{max} (MeCN) 228 nm (ε 28200). ^1H n.m.r. δ_H 1.17, 1.20, (1-Me,8-Me); 1.27, t-Bu; 3.10, H2,H7; 6.62, H5; 6.9-7.4, phenyls. ^{13}C n.m.r. δ_C 10.1, 1-Me,8-Me; 29.1, Bu^t; 36.0, C_q(Bu); 53.3, 53.5, (C2,C7); 56.8, 56.9 (C1,C8); 127.9, 128.3, 129.2, phenyl carbons; 132.9, 133.1, ipso phenyl carbons; 136.4, C5; 143.7, 143.9, (C9,C10); 163.7, C4; 195.9, 196.7, (C3,C6); 203.2, C11 (Found: C, 81.8; H, 6.8. $C_{29}H_{28}O_3$ requires: C, 82.1; H, 6.7%).

v) Reaction of hemicyclone with 1,4-naphthoquinone **(13e)** gave endo-1,12-dimethyl-13,14-diphenyltetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]-pentadeca-4,6,8,13-tetraene-3,10,15-trione **(31e)** (5.1 g) which was recrystallised from benzene-dichloromethane as colourless prisms, m.p. 196-198°. ν_{max} 1795, 1770, 1680, 1670 cm^{-1}, λ_{max} (MeCN) 310 nm (ε 500), 250 (3600), 219 (8400). ^1H n.m.r.

δ_H 1.58, 1-Me,12-Me; 3.52, H2,H8; 6.3-6.6, (4H), 6.7-7.1, (6H), phenyls; 7.7, H6,H7; 8.0, H5,H8. ^{13}C n.m.r. δ_C 12.0, 1-Me,12-Me; 53.0, C2,C11; 59.4, C1,C12; 127.3, 127.4, 127.9, 129.4, (C5,C8, phenyl carbons); 133.1, ipso phenyl carbons; 134.4, C6,C7; 137.1, C4,C9; 141.5, C13,C14; 194.4, C3,10; 199.9, C15 (Found; C, 83.3; H, 5.3. $C_{29}H_{22}O_3$ requires: C, 83.2; H, 5.3%).

vi) Reaction of hemicyclone with cyclohex-2-eneone (73) gave endo-1,8-dimethyl-9,10-diphenyltricyclo[6,2,1,$0^{2,7}$]undec-9-ene-3,11-dione (40) (0.85 g) which was recrystallised from hexane-dichloromethane as colourless prisms, m.p. 165°. ν_{max} 1780, 1700 cm^{-1}. λ_{max} (MeCN) 262 nm (ε 8800), 225 (15200). ^1H n.m.r. δ_H 1.37, 1.48, (1-Me,8-Me), 1.7-3.0, (8H); 6.8-7.3, phenyls. ^{13}C n.m.r. δ_C 11.4, 12.4, (1-Me,8-Me); 20.6, C5; 24.6, C6; 40.4, C4; 46.3, C7; 53.2, C2; 56.9, 57.2, (C1,C8); 127.0, 127.7, 127.9, 129.6, phenyl carbons; 134.6, 135.1, ipso phenyl carbons; 143.7 C9,C10; 203.6, C11; 210.5, C3 (Found: $M^{+\cdot}$, 356.1766; C, 84.0; H, 6.9. $C_{25}H_{24}O_2$ requires: $M^{+\cdot}$, 356.1776; C, 84.2; H, 6.8%). Crystals from the mother liquor were recrystallised several times from hexane-dichloromethane to give exo-1,8-dimethyl-9,10-diphenyltricyclo[6,2,1,$0^{2,7}$]undec-9-ene-3,11-dione (41) (0.65 g) which was as colourless prisms, m.p. 161°. ν_{max} 1770, 1705 cm^{-1}. λ_{max} (MeCN) 255 nm (ε 12600), 218 (19800). ^1H n.m.r. δ_H 1.17,1.27, (1-Me,8-Me), 1.5-3.0, (8H); 6.8-7.3, phenyls. ^{13}C n.m.r. δ_C 8.9, 10.2, (1-Me,8-Me); 19.7, C5; 24.5, C6; 38.9, C4; 42.1, C7; 54.7, C2; 54.9, 55.1 (C1,C8); 127.4, 128.0, 129.0 phenyl carbons; 133.4, 134.1, ipso phenyl carbons; 144.1, C9,C10; 207.0, C11; 211.1, C3 (Found: $M^{+\cdot}$,

356.1763; C, 83.7; H, 6.9. $C_{25}H_{24}O_2$ requires: $M^{+\cdot}$, 356.1776; C, 84.2; H, 6.8%).

Enedione reductions

i) A mixture of **(20)** (1 g) and Pd/C (10%, 0.12 g) in ethyl acetate (125 ml) was agitated in a hydrogen atmosphere (2 atm). After the solution became colourless (36 hr) the catalyst was removed by filtration and after removal of solvent the residue was recrystallised from dichloromethane-hexane to give endo-1,8-dimethyl-9,10-diphenyltricyclo[6,2,1,$0^{2,7}$]undec-9-ene-3,6,11-trione **(38)** (0.95 g) as colourless prisms, m.p. 185-186°. ν_{max} 1775, 1700 cm^{-1}. λ_{max} (MeCN) 260 nm (ε 6550), 223 (11500). ^1H n.m.r. δ_H 1.55, 1-Me,8-Me; 2.70, $(H4)_2$,$(H5)_2$; 3.2, H2,H7; 6.7-7.3, phenyls. ^{13}C n.m.r. δ_C 12.1, 1-Me,8-Me; 38.5, C4,C5; 54.7, C2,C7; 57.9, C1,C8; 127.7, 128.3, 129.3, phenyl carbons; 133.7, ipso phenyl carbons; 142.8, C9,C10; 200.3, C11; 205.9, C3,C6 (Found: $M^{+\cdot}$, 370.1599; C, 80.9; H, 6.2. $C_{25}H_{22}O_3$ requires: $M^{+\cdot}$, 370.1568; C, 81.1; H, 6.0%).

ii) To a solution of **(8a)**[2] (1.0 g, 6 mmole) in acetone (50ml) was added freshly ground potassium iodide (4.0 g, 24 mmole) and concentrated hydrochloric acid (2ml). The solution became dark and was stirred (5 min), poured into ether (100 ml) and washed several times with aqueous sodium thiosulphate (0.1 M) and water. The organic phase was dried over sodium sulphate and after removal of solvent gave an oil which was crystallised from benzene to give endo-anti-endo-pentacyclo[10,2,1,$1^{5,8}$,$0^{2,11}$,$0^{4,9}$] hexadeca-6,13-diene-3,10-dione **(44)** (50 mg) as needles, m.p. 158° (lit.[81] 159-160°). ^1H n.m.r. δ_H 1.4, AB_q, $W_{h/2}$ 8Hz, $(H15)_2$,

$(H16)_2$; 2.8, $W_{h/2}$ 5Hz, H2,H4,H9,H11; 3.3, $W_{h/2}$ 6Hz, H1,H5,H8,H12; 6.2, $W_{h/2}$ 4Hz, H6,H7,H13,H14. ^{13}C n.m.r. δ_C 48.2, (4C); 49.6, C15,C16; 53.2, (4C); 136.4, C6,C7,C13,C14; 212.4, C3,C10. The mother liquor was absorbed onto neutral alumina (100 ml) and elution with chloroform gave endo-tricyclo[6,2,1,$0^{2,7}$]undec-9-ene-3,6-dione **(43)**[143] (0.5 g) as an oil. ν_{max} (smear) 1705 cm^{-1}. ^1H n.m.r. (CCl_4) δ_H 1.43, $W_{h/2}$ 6Hz, $(H11)_2$; 2.38, $W_{h/2}$ 30Hz, $(H4)_2$,$(H5)_2$; 3.12, $W_{h/2}$ 6Hz, H1,H8; 3.40, $W_{h/2}$ 6Hz, H2,H7; 6.17, t, J 2Hz, H9,H10. ^{13}C n.m.r. (CCl_4) δ_C 37.5, C4,C5; 47.1, C1,C8; 48.3, C11; 51.4, C2,C7; 136.4, C9,C10; 206.8, C3,C6 (Found: $M^{+\cdot}$, 176.0840. $C_{11}H_{12}O_2$ requires: $M^{+\cdot}$, 176.0837).

Epoxidation reactions of enedione **(20)**

i) A solution of **(20)** (1 g) and m-chloroperbenzoic acid (1 g) in chloroform was kept at room temperature for 2 days. The mixture was poured into dilute aqueous sodium hydroxide. The organic phase was washed several times with aqueous sodium hydroxide, water and dried with sodium sulphate. The solvent was removed and the residue recrystallised from dichloromethane-ethanol to give exo-1,8-dimethyl-11,12-diphenyl-9-oxatricyclo[6,2,2,$0^{2,7}$]dodeca-4,11-diene-3,6,10-trione **(51)** (0.6 g) which was recrystallised from ethanol-dichloromethane, m.p. 163-165°. ν_{max} 1760, 1670 cm^{-1}. λ_{max} 220 nm (ε 20800). ^1H n.m.r. δ_H 1.37, 1.65, (1-Me,8-Me); 3.25, $J_{2,7}$ 8Hz, H2; 3.60, $J_{7,2}$ 8Hz, H7; 6.6-7.3, phenyls, H4, H5. ^{13}C n.m.r. δ_C 16.6, 21.6, (1-Me,8-Me); 49.5, C2; 49.8, C1; 55.8, C7; 83.0, C8; 127.7, 128.1, 129.1, phenyl carbons; 134.2, ipso phenyl carbons; 142 2, 143.2, (C4,C5); 142.5, 143.0, (C11,C12); 173.6, C10; 193.6, 194.0, (C3,C6)

(Found: $M^{+\cdot}$, 384.1369; C, 78.2; H, 5.3. $C_{25}H_{20}O_4$ requires: $M^{+\cdot}$, 384.1362; C, 78.1; H, 5.2%).

ii) To a solution of **(20)** (150 mg) in acetone (10 ml) was added aqueous sodium carbonate (0.2 ml, 20%) and hydrogen peroxide (0.3 ml, 30%). Over a period of 5 hr the solution changed from a pale yellow to pale orange colour with evolution of carbon monoxide. The mixture was poured into water (25 ml) and the products extracted with dichloromethane (3 x 10 ml). The combined organic phase was dried with sodium sulphate and after removal of solvent the residue was absorbed onto silica on a radial chromatograph. Elution with chloroform gave 2,3-epoxy-5,8-dimethyl-6,7-diphenyl-1,2,3,4-tetrahydronaphthalene-1,4-dione **(53)** which was recrystallised from ethanol as yellow needles (50 mg), m.p. 221-222°. ν_{max} 1695 cm^{-1}. λ_{max} (MeCN) 325 nm (ε 5900), 249 (30700), 216 (26700). ^1H n.m.r. δ_H 2.23, 5-Me,8-Me; 4.07, H2,H3; 6.7-7.3, phenyls. ^{13}C n.m.r. δ_C 18.4, 5-Me,8-Me; 55.6, C2,C3; 194.8, C1,C4. (Found: $M^{+\cdot}$, 354.1267; C, 81.2; H, 5.1. $C_{24}H_{18}O_3$ requires: $M^{+\cdot}$, 354.1259; C, 81.3; H, 5.1%). Further elution with methanol-chloroform (1:9) gave 2-hydroxy-5,8-dimethyl-6,7-diphenyl-1,2,3,4-tetrahydronaphthalene-1,4-dione **(52)** which was recrystallised from ethanol as an amorphous solid (80 mg), m.p. 161-163°. ν_{max} 3400, 1685 cm^{-1}. λ_{max} (MeCN) 320 nm (ε 4700), 239 (34700). ^1H n.m.r. δ_H 2.33, $W_{h/2}$ 3Hz, 5-Me,8-Me; 2.92, d,d, $J_{3b,3a}$ 15Hz, $J_{3b,2}$ 12Hz, H3b; 3.52, d,d, $J_{3a,3b}$ 15Hz, $J_{3a,2}$ 7Hz, H3a; 4.83, d,d, $J_{2,3a}$ 7Hz, $J_{2,3b}$ 12Hz, H2; 6.7-7.3, phenyls. ^{13}C n.m.r. δ_C 19.4, 19.9, (5-Me,8-Me); 49.1, C3; 72.5, C2; 126.8, 127.7, 127.8, 129.3, 129.5, 129.6, phenyl carbons, C5,C6,C7,C8; 136.1, 139.6, ipso

phenyl carbons, 200.9, (C1,C4) (Found: $M^{+\cdot}$, 356.1411. $C_{24}H_{20}O_3$ requires: $M^{+\cdot}$, 356.1412).

iii) To a stirred solution of **(20)** (500 mg) and excess tetracyanoethylene (200 mg) in acetone (15 ml) was added a solution of sodium carbonate (0.8 ml, 20%) and hydrogen peroxide (1.2 ml, 30%). Bubbling accompanied the peroxide/carbonate addition but subsided after 5 min. The reaction mixture was poured into water and the organic phase washed several times with dilute aqueous sodium hydroxide, water and dried with sodium sulphate. After removal of solvent the residue was absorbed onto silica on a radial chromatograph and elution with ether-petroleum ether (1:1) gave endo-anti-1,9-dimethyl-10,11-diphenyl-12-(anti-cyano-syn-hydroxy)-5-oxatetracyclo[7,2,1,$0^{2,8}$,$0^{4,6}$]dodec-10-ene-3,7-dione **(55)** (350 mg) which was recrystallised from methanol-dichloromethane as colourless prisms, m.p. 209-211°. ν_{max} 3400, 2350, 1720 cm^{-1}. λ_{max} (MeCN) 218 nm (ε 17200). ^1H n.m.r. δ_H 1.55, 1-Me, 9-Me; 3.68, H2,H4,H6,H8; 6.8-7.3, phenyls. ^{13}C n.m.r. δ_C 13.5, 1-Me,9-Me; 53.2, C2,C8; 58.5, C4,C6; 60.2, C1,C9; 90.6, C12; 119.4, cyano carbon; 127.3, 127.8, 129.6, phenyl carbons; 134.6, ipso phenyl carbons; 146.2, C10,C11; 202.4, C3,C7 (Found: $M^{+\cdot}$, 411.1456; C, 75.6; H, 5.4, N, 3.3. $C_{26}H_{21}NO_4$ requires: $M^{+\cdot}$, 411.1470; C, 75.9; H, 5.1; N, 3.4%).

iv) To a stirred solution of **(20)** (615 mg) in acetone (20 ml) was added an aqueous solution of sodium carbonate (0.8 ml, 5%) and hydrogen peroxide (1.2 ml, 30%) and the mixture stirred at room temperature for 5 min. The reaction mixture was poured into dilute sodium bisulphate solution, and the product extracted

with dichloromethane (3 x 20 ml). The organic phase was then washed with brine, dried with sodium sulphate and the solvent removed under reduced pressure. The residue was recrystallised from dichloromethane-ethanol to give endo-anti-1,9-dimethyl-10,11-diphenyl-5-oxatetracyclo-[7,2,1,$0^{2,8}$,$0^{4,6}$]dodec-10-ene-3,7,12-trione **(50)** as colourless needles (350 mg), m.p. 190-191°. ν_{max} 1765, 1720 cm^{-1}. λ_{max} (MeCN) 238 nm (ε 7300), 218 (21800). ^1H n.m.r. δ_H 1.50, 1-Me,9-Me; 3.60, H2,H8; 3.67, H4,H6; 6.8-7.3, phenyls. ^{13}C n.m.r. δ_C 12.4, 1-Me,9-Me; 52.6, C2,C8; 55.3, C1,C9; 58.8, C4,C6; 127.3, 127.8, 130.0, phenyl carbons; 134.7, ipso phenyl carbons; 144.2, C10,C11; 199.7, C12; 200.9, C3,C7 (Found: $M^{+}\cdot$, 384.1316; C, 78.0; H, 5.3. $C_{25}H_{20}O_4$ requires: $M^{+}\cdot$, 384.1362; C, 78.1; H, 5.2%).

Alternatively this compound was prepared as follows: a solution of hemicyclone (190 mg, 0.73 mmole) and benzoquinone epoxide[93] (90 mg, 0.73 mmole) in benzene (7 ml) was heated under reflux for 30 hr. The solvent was removed and the residue was absorbed onto silica on a radial chromatograph and elution with ether-petroleum ether (1:1) yielded an epoxide **(55)** (66 mg) identical with the above sample. Elution with ether gave a trace quantity of the exo-anti-epoxide, m.p. 155-156°. ^1H n.m.r. δ_H 1.45, methyls; 3.15, H2,H8; 3.65, H4,H6; 7.1, $W_{h/2}$ 14Hz, phenyls.

Decarbonylation of enedione **(31b)**

To a stirred solution of **(31b)** (1.0 g) in acetone (30 ml) was added an aqueous solution of sodium carbonate (1.0 ml, 5%) and hydrogen peroxide (1.5 ml, 30%) and the mixture was stirred at room temperature for 5 min and following workup (as for iv)

above) the residue was recrystallised from ethanol-dichloromethane to give 2,3,5,8-tetramethyl-6,7-diphenylnaphthalene-1,4-dione **(56)** as yellow needles (0.44 g), m.p. 178-180°. ν_{max} 1670 cm^{-1}. λ_{max} (MeCN) 357 nm (ε 3500), 257 (18600), 221 (24600). ^1H n.m.r. δ_H 2.17, 5-Me,8-Me; 2.40, 2-Me,3-Me; 7.0, $W_{h/2}$ 12Hz, phenyls. ^{13}C n.m.r. δ_C 12.9, 5-Me,8-Me; 20.2, 2-Me,3-Me; 126.5, 127.6, 129.6, phenyl carbons; 131.7, 136.8, 140.2, quaternary phenyl carbons; 148.0, C2,C3; 188.2, C1,C4 (Found: $M^{+}\cdot$, 366.1609; C, 84.7; H, 6.1. $C_{26}H_{22}O_2$ requires: $M^{+}\cdot$, 366.1620; C, 85.1; H, 6.1%).

Photolysis of Diels-Alder adducts

General procedure: Solutions of the adducts were irradiated with a low-pressure 450W Hg lamp (Hanovia) (pyrex filter) in quartz reaction vessels submerged in waterbaths (0-35°) for periods of at least 0.5 hr. Reaction progress was in each case monitored by ^1H n.m.r. spectroscopy. All photolyses were carried out in a nitrogen atmosphere.

i) A solution of **(20)** (500 mg) in benzene (150 ml) was irradiated for 1.5 hr. The solvent was removed and the product mixture was absorbed onto silica on a radial chromatographic plate and elution with ether-petroleum ether (1:1) gave 5,7-dimethyl-3,4-diphenyl-2-oxapentacyclo[6,4,0,$0^{1,4}$,$0^{3,7}$,$0^{5,9}$]dodec-11-ene-6,10-dione **(29)** (70 mg) which was recrystallised from ethanol as colourless needles, m.p. 185-186° (lit.[48] 180-225°). ν_{max} 1770, 1660 cm^{-1}. λ_{max} ($CHCl_3$) 261 nm (ε 16900). ^1H n.m.r. δ_H 0.88, 5-Me; 1.25, 7-Me; 3.00, d, $J_{8,9}$ 3Hz, H8; 3.20, m, $W_{h/2}$ 4Hz, H9; 6.31, d,d,

$J_{11,9}$ 1.5Hz, $J_{11,12}$ 10Hz, H11; 6.6-7.3, phenyls; 7.73, d, $J_{12,11}$ 10Hz, H12. ^{13}C n.m.r. δ_C 8.3, 8.8, (5-Me,7-Me); 57.0, 58.6, (C5,C7); 64.0, 65.1, (C8,C9); 82.7, C4; 95.3, 99.7, (C1,C3); 148.6, C12; 195.2, C10; 211.0, C6 (Found: $M^{+}\cdot$, 368.1399. $C_{25}H_{20}O_3$ requires: $M^{+}\cdot$, 368.1412). Further elution with chloroform gave 3,5-dimethyl-2,6-diphenyl-pentacyclo[5,4,0,$0^{2,6}$,$0^{3,10}$,$0^{5,9}$]undecan-4,8,11-trione **(21)** (280 mg) which was recrystallised from hexane-dichloromethane as colourless prisms, m.p. 267-268° (lit.[48] 270°). ν_{max} 1760, 1735 cm^{-1}, λ_{max} (MeCN) 216 nm (ε 13000). ^{1}H n.m.r. δ_H 1.07, 3-Me,5-Me; 2.92, $W_{h/2}$ 4Hz, H9,H10; 3.67, $W_{h/2}$ 4Hz, H1,H7; 6.7-7.4, phenyls. ^{13}C n.m.r. δ_C 11.0, 3-Me,5-Me; 46.3, C1,C7; 51.8, C2,C6; 55.0, C9,C10; 58.0, C3,C5; 127.3, 128.0, phenyl carbons; 134.2, ipso phenyl carbons; 206.8, C8,C11; 211.7, C4 (Found: $M^{+}\cdot$, 368.1402. $C_{25}H_{20}O_3$ requires: $M^{+}\cdot$, 368.1412).

ii) A solution of **(31b)** (500 mg) in benzene (150 ml) was irradiated for 1.0 hr. The solvent was removed to give a residue from which the major product 1,3,5,7-tetramethyl-2,6-diphenylpentacyclo-[5,4,0,$0^{2,6}$,$0^{3,10}$,$0^{5,9}$]undecan-4,8,11-trione **(33b)** which readily recrystallised as colourless prisms from hexane-dichloromethane, (231 mg) m.p. 234-235°. ν_{max} 1755, 1740 cm^{-1}. λ_{max} (MeCN) 217 nm (ε 12600). ^{1}H n.m.r. δ_H 1.08, 3-Me,5-Me; 1.27, 1-Me,7-Me; 2.95, H9,H10; 6.7-7.2, phenyls. ^{13}C n.m.r. δ_C 12.2, 13.0, methyls; 52.1, C1,C7; 54.5, C9,C10, 56.6, C3,C5; 60.1, C2,C6; 126.8, 127.4, 129.4, phenyl carbons; 135.9, ipso phenyl carbons; 209.9, C8,C11; 210.4, C4 (Found: $M^{+}\cdot$, 396.1724; C, 82.0; H, 6.0. $C_{27}H_{24}O_3$ requires: $M^{+}\cdot$, 396.1725; C, 81.8; H, 6.1%). The

mother liquor was recrystallised several times to give 5,7,11,12-tetramethyl-3,4-diphenyl-2-oxapentacyclo-[6,4,0,$0^{1,4}$,$0^{3,7}$,$0^{5,9}$]dodec-11-ene-6,10-dione **(34b)** as colourless prisms from ethanol (54 mg), m.p. 155-158°. ν_{max} 1775, 1650 cm^{-1}. λ_{max} (MeCN) 268 nm (ε 5700), 220 (14200). ^{1}H n.m.r. δ_H 0.87, 5-Me; 1.17, 7-Me; 1.90, 1.97, ^{5}J 1.5Hz, (11-Me,12-Me); 2.87, d, $J_{8,9}$ 2.5Hz, H8; 3.22, d, $J_{9,8}$ 2.5Hz, H9; 6.4-6.7, (2H), 6.9-7.4, (8H), phenyls. ^{13}C n.m.r. δ_C 8.0, 8.5, (5-Me,7-Me); 11.0, 11-Me; 14.7, 12-Me; 56.4, 59.2, (C5,C7); 61.8, 64.4, (C8,C9); 81.7, C4; 98.2, C1,C3; 125.7, 127.2, 127.8, 128.6, 128.8, phenyl carbons; 131.7, 133.7, 133.9, (ipso phenyl carbons,C11); 154.0, C12; 194.4, C10; 211.2, C6 (Found: $M^{+}\cdot$, 396.1724; C, 81.7; H, 6.2. $C_{27}H_{24}O_3$ requires: $M^{+}\cdot$, 396.1725; C, 81.8; H, 6.1%)

iii) A solution of **(31c)** (800 mg) in benzene (175 ml) was irradiated for 0.5 hr. The solvent was removed to give a residue from which the major isomer 1,3,5-trimethyl-2,6-diphenylpentacyclo-[5,4,0,$0^{2,6}$,$0^{3,10}$,$0^{5,9}$]undecane-4,8,11-trione **(33c)** was recrystallised as colourless prisms from hexane-dichloromethane, (460 mg) m.p. 232-232.5°. ν_{max} 1765, 1740 cm^{-1}. λ_{max} (MeCN) 219 nm (ε 15500). ^{1}H n.m.r. δ_H 0.97, 1.10, (3-Me,5-Me); 1.57, 1-Me; 2.90, $W_{h/2}$ 1.5Hz, H9,H10; 3.18, d, J 2Hz, H7; 7.0, m, $W_{h/2}$ 18Hz, phenyls. ^{13}C n.m.r. δ_C 11.5, 12.1, (3-Me,5-Me); 17.6, 1-Me; 51.4, 52.4, 53.6, 54.8, 55.4, 56.1, 60.5, (C1,C2,C3,C5,C6,C7,C9,C10); 126.8, 127.5, 127.6, 128.1, 128.6, phenyl carbons; 135.2, 135.3, ipso phenyl carbons; 207.3, 208.9, (C8,C11); 211.2, C4 (Found: $M^{+}\cdot$, 382.1562; C, 81.6; H, 5.9. $C_{26}H_{22}O_3$ requires: $M^{+}\cdot$, 382.1569; C, 81.7; H, 5.8%). The residue

from the mother liquor was repeatedly recrystallised to give the minor isomer 5,7,12-trimethyl-3,4-diphenyl-2-oxapentacyclo-[6,4,0,$0^{1,4}$,$0^{3,7}$,$0^{5,9}$]dodec-11-ene-6,10-dione **(34c)** (150 mg) as colourless prisms from ethanol-dichloromethane, m.p. 175-176°. ν_{max} 1765, 1655 cm^{-1}. λ_{max} (MeCN) 261 nm (ε 5000), 218 (12900). ^1H n.m.r. δ_H 0.92, 5-Me; 1.20, 7-Me; 2.03, d, ^4J 1.5Hz, 12-Me; 3.00, d, $J_{8,9}$ 2.5Hz, H8; 3.20, $W_{h/2}$ 5Hz, H9; 6.15, $W_{h/2}$ 4Hz, H11; 6.6-6.9, (2H), 6.9-7.5, (8H), phenyls. ^{13}C n.m.r. δ_C 8.0, 8.6, (5-Me,7Me); 18.0, 12-Me; 56.6, 59.2, (C5,C7); 62.7, 65.0, (C8,C9); 82.2, C4; 98.1, 98.6, (C1,C3); 125.6, 127.4, 127.8, 127.9, 128.6, 128.8, phenyl carbons,C11; 131.3, 133.4, ipso phenyl carbons; 161.4, C12; 194.9, C10; 210.8, C6 (Found: $M^{+}\cdot$, 382.1562; C, 81.1; H, 5.8. $C_{26}H_{22}O_3$ requires: $M^{+}\cdot$, 382.1569; C, 81.7; H, 5.8%).

iv) A solution of **(31d)** (165 mg) in benzene (50 ml) was irradiated for 0.5 hr. The solution was concentrated under reduced pressure to give an oil which was absorbed onto silica on a radial chromatograph. Elution with ether-petroleum ether (1:9) gave 11-<u>tert</u>-butyl-5,7-dimethyl-3,4-diphenyl -2-oxapentacyclo[6,4,0,$0^{1,4}$,$0^{3,7}$,$0^{5,9}$]dodec-11-ene-6,10-dione **(35d)** as colourless needles from ethanol-dichloromethane, (28 mg) m.p. 165°. ν_{max} 1770, 1670 cm^{-1}. λ_{max} (MeCN) 261 nm (ε 8200), 220 (20000). ^1H n.m.r. δ_H 0.85, 5-Me; 1.20, 7-Me; 1.25, Bu^t; 2.82, d, $J_{9,8}$ 3Hz, H9; 3.13, d, $J_{8,9}$ 3Hz, H8; 6.6-6.9, (2H), 6.9-7.5, (8H), phenyls; 7.43, s, H12. ^{13}C n.m.r. δ_C 8.2, 8.7, (5-Me,7-Me); 28.8, Bu^t; 34.7, C_q(Bu); 56.8, 58.6, (C5,C7); 62.4, 65.1, (C8,C9); 82.8, C4; 95.8, 99.5, (C1,C3); 125.9, 127.3, 127.7, 128.5, 129.5, phenyl carbons; 131.6, 133.3, ipso phenyl carbons; 140.9, C12; 149.9, C11; 194.5, C10; 211.5, C6 (Found:

$M^{+}\cdot$, 424.2028; C, 82.4; H, 6.5. $C_{29}H_{28}O_3$ requires: $M^{+}\cdot$, 424.2038; C, 82.1; H, 6.7%). Elution with ether-petroleum ether (1:3) gave 12-tert-butyl-5,7-dimethyl-3,4-diphenyl -2-oxapentacyclo[6,4,0,$0^{1,4}$,$0^{3,7}$,$0^{5,9}$]dodec-11-ene-6,10-dione **(34d)** which was recrystallised as colourless prisms from ethanol-dichloromethane, (63 mg) m.p. 174°. ν_{max} 1775, 1665 cm^{-1}. λ_{max} (MeCN) 255 nm (ε 6900), 221 (20000). ^{1}H n.m.r. δ_H 0.97, Bu^t; 0.98, 5-Me; 1.07, 7-Me; 2.98, d, $J_{8,9}$ 2.5Hz, H8; 3.20, m, $J_{9,8}$ 2.5Hz, J 1Hz, H9; 6.15, m, J 1Hz, H11; 6.6-6.9, (2H), 6.9-7.5, (8H), phenyls. ^{13}C n.m.r. δ_C 7.8, 8.5, (5-Me,7-Me); 27.5, Bu^t; 36.7, C_q(Bu); 56.8, 60.0, (C5,C7); 64.3, 65.1, (C8,C9); 82.2, C4; 97.5, 100.4, (C1,C3); 123.9, C11; 125.0, 127.4, 127.5, 127.6, 128.5, 128.7, 129.6, phenyl carbons; 132.0, 134.1, ipso phenyl carbons; 171.2, C12; 196.3, C10; 210.9, C6 (Found: $M^{+}\cdot$, 424.2028; C, 81.4; H, 6.8. $C_{29}H_{28}O_3$ requires: $M^{+}\cdot$, 424.2038; C, 82.1; H, 6.7%).

v) A solution of **(31e)** (1.0g) in benzene (200 ml) was irradiated as above for 2.5 hr. Examination of proton n.m.r. spectra showed no reaction to have occured.

vi) A solution of **(38)** (200 mg) in benzene (30 ml) was irradiated for 1.0 hr. The solvent was removed and the residue absorbed onto silica on a radial chromatograph. Elution with ether gave 5,7-dimethyl-3,4-diphenyl -2-oxapentacyclo[6,4,0,$0^{1,4}$,$0^{3,7}$,$0^{5,9}$]dodecane-6,10-dione **(39)** (130 mg) which was recrystallised from ethanol-dichloromethane as colourless needles, m.p. 191-192°. ν_{max} 1770, 1700 cm^{-1}. λ_{max} ($CHCl_3$) 277 nm (ε 4100), 240 (6000). ^{1}H n.m.r. δ_H 1.03, 5-Me; 1.17, 7-Me; 2.90, $J_{8,9}$ 2Hz, H8; 3.00,

$J_{9,8}$ 2Hz, H9; 6.7-7.0, (2H), 7.0-7.5, (8H), phenyls. ^{13}C n.m.r. δ_C 8.2, 9.2, (5-Me,7-Me); 21.1, C12; 36.8, C11; 55.7, C9; 55.9, 59.2, (C5,C7); 60.9, C8; 75.0, C4; 96.3, 97.4, (C1,C3); 125.2, 127.2, 128.3, 128.5, 129.3, phenyl carbons; 131.6, 133.6, ipso phenyl carbons; 208.6, C10; 210.9, C6 (Found: $M^{+\cdot}$ - CO, 342.1598; C, 80.6; H, 6.2. $C_{25}H_{22}O_3$ requires: $M^{+\cdot}$ - CO, 342.1619; C, 81.1; H, 6.0%).

An ethyl acetate (50 ml) solution of the oxetane **(29)** (30 mg) and palladium/charcoal (5 mg, 10%) was agitated under a hydrogen atmosphere (2 atm) for 24 hr. The solution was filtered (Celite) and concentrated at reduced pressure to give a product **(39)** with identical spectral properties to those described above.

vii) A solution of **(40)** (60 mg) in benzene (25 ml) was irradiated as above for 0.5 hr. The solvent was removed to give an oil which was recrystallised from ethanol to give 5,7-dimethyl-3,4-diphenyl-2-oxapentacyclo-[6,4,0,$0^{1,4}$,$0^{3,7}$,$0^{5,9}$,]dodecan-6-one **(42)** (20 mg) which was recrystallised from ethanol-dichloromethane, m.p. 142-143°. ν_{max} 1755 cm^{-1}. λ_{max} ($CHCl_3$) 277 nm (ε 4900). ^1H n.m.r. δ_H 0.90, 5-Me; 1.30, 7-Me; 1.5-3.0, br m, (8H); 7.1, $W_{h/2}$ 3Hz, phenyls. ^{13}C n.m.r. δ_C 8.9, 9.5, (5-Me,7-Me); 20.8, C11; 25.4, C10; 28.6, C12; 51.0, C9; 61.0, C8; 55.9, 57.6, (C5,C7); 74.7, C4; 97.5, C1,C3; 126.6, 127.5, 127.9, 129.2, phenyl carbons; 133.3, ipso phenyl carbons; n.o. C6 (Found: $M^{+\cdot}$, 356.1770; C, 83.6; H, 6.8. $C_{25}H_{24}O_2$ requires: $M^{+\cdot}$, 356.1776; C, 84.2; H, 6.8%).

viii) A solution of **(43)** (370 mg) in acetone (50 ml) was irradiated as above for 2 hr. The product mixture was shown to be complex with polymeric material predominating.

ix) A solution of **(50)** (500 mg) in benzene (175 ml) was irradiated for 3.5 hr. The solution was concentrated at reduced pressure to give a dark-red oil which was shown to be a complex mixture of products. Absorption onto silica on a radial chromatograph and elution with ether-petroleum ether (1:1) gave 5,7-dimethyl-3,4-diphenyl-2,12-dioxahexacyclo-[6,5,0,$0^{1,4}$,$0^{3,7}$,$0^{5,9}$,$0^{11,13}$]tridecane-6,10-dione **(57)** (70 mg) which was recrystallised from hexane-dichloromethane as colourless prisms, m.p. 205-206°. ν_{max} 1775, 1770 cm^{-1}. λ_{max} (MeCN) 258 nm (ε 825), 221 (11400). ^1H n.m.r. δ_H 0.82, 5-Me; 1.17, 7-Me; 3.00, $W_{h/2}$ 4Hz, H9; 3.22, d, $J_{8,9}$ 2Hz, H8; 3.70, br d, $J_{11,13}$ 5Hz, H11; 3.98, d, $J_{13,11}$ 5Hz, H13;; 6.6-7.0, (2H), 7.0-7.5, (8H), phenyls. ^{13}C n.m.r. δ_C 8.2, 8.7, (5-Me,7-Me); 51.3, 51.5, (C8,C9); 56.7, 57.6, (C5,C7); 58.7, 60.6, (C11,C13); n.o., C4; 95.6, 98.8, (C1,C3); 125.7, 127.7, 128.3, 128.7, 128.8, 129.1, phenyl carbons; 131.1, 133.0, ipso phenyl carbons; 200.5, C10; 210.2, C6 (Found: $M^{+}\cdot$, 384.1357; C, 77.7; H, 5.3. $C_{25}H_{20}O_4$ requires: $M^{+}\cdot$, 384.1362; C, 78.1; H, 5.2%). Elution with ether gave endo-1,9-dimethyl-10,11-diphenyl-4-oxatricyclo-[7.2.1.$0^{2,8}$]dodeca-5,10-diene-3,7,12-trione **(58)** (20 mg) which was recrystallised from benzene as colourless prisms, m.p. 235°. ^1H n.m.r. δ_H 0.83, 1-Me; 1.30, 9-Me; 3.0, d,d, $J_{8,2}$ 11Hz, $J_{8,6}$ 2Hz, H8; 3.2, d, $J_{2,8}$ 11Hz, H2; 3.93, d,d, $J_{6,5}$ 10Hz, $J_{6,8}$ 2Hz, H6; 5.9, d, $J_{5,6}$ 10Hz, H5; 7.0, $W_{h/2}$ 10Hz, phenyls.

^{13}C n.m.r. δ_C 169.3; 206.0; 208.7, (C7,C12) (Found: $M^{+\cdot}$, 384.1357. $C_{25}H_{20}O_4$ requires: $M^{+\cdot}$, 384.1362).

Cyclopentadiene-naphthoquinone cage diene **(37)**

The Diels-Alder adduct of cyclopentadiene and 1,4-naphthoquinone in benzene (1% w/v) contained in a quartz reaction vessel submerged in a water bath (0-35°) was irradiated with a low-pressure 450-W Hg lamp (Hanovia) (Pyrex filter) for 4 min after which time the solvent was removed under reduced pressure to give the caged photoproduct **(37)** in high yield as a crystalline solid, m.p. 108-110° (lit.[79] 111-112°). ν_{max} 1740 cm^{-1}. ^1H n.m.r. δ_H 1.76, d, $J_{15b,15a}$ 11.3Hz, H15b; 1.99, d, $J_{15a,15b}$ 11.3Hz, H15a; 2.80, m, H2,H11; 2.99, m, H1,H12; 3.35, m H13,H14; 5.38, br d, $J_{6,5}$ 8.1Hz, H6,H7; 5.97, br d, $J_{5,6}$ 8.1Hz, H5,H8). ^{13}C n.m.r. δ_C 38.9, C15; 44.2, C1,C12; 50.2, C4,C9; 51.6, C13,C14; 54.6, C2,C11; 119.8, C5,C8; 124.7, C6,C7; 210.4, C3,C10) (Found: $M^{+\cdot}$, 224.0836. $C_{15}H_{12}O_2$ requires: $M^{+\cdot}$, 224.0837) Recrystallisation of the crude solid (2.0 g) from ethanol-dichloromethane gave colourless prisms (1.3 g) of the mono-hemiacetal **(62)**, m.p. 104-107°; ν_{max} 3400, 3000, 1740 cm^{-1} ^1H n.m.r. δ_H 1.08, t, ^3J 7.5Hz, methyl protons; 1.39, br d, $J_{15b,15a}$ 11.0Hz, H15b; 1.76, br d, $J_{15a,15b}$ 11.0Hz, H15a; 2.53, d,d,d, J 1.8Hz, J 4.2Hz, J 9.8Hz, (1H); 2.68, m, (2H); 2.90, m, (2H); 3.07, d,d,d, J 1.8Hz, J 4.9Hz, J 8.7Hz, (1H); 3.61, m, methylene protons; 5.56, br d, 5.67, br d, $J_{5,8}$ 9.9Hz, (H5,H8); 5.89, d,d,d, J 1.2Hz, J 5.4Hz, J 9.6Hz, 5.95 d,d,d, J 1.5Hz, J 6.0Hz, J 9.6Hz, (H6,H7). ^{13}C n.m.r. δ_C 36.5, C15; 42.5, 45.5, (C1,C12); 50.1, 50.6, (C13,C14); 56.2, 59.7, (C2,C11); 103.7, C3 121.3, 123.0 (2C), 123.8, (C5,C6,C7,C8); 212.4, C10 (Found: C, 75.5; H, 6.7. $C_{17}H_{18}O_3$ requires: C, 75.5; H, 6.7%).

Diels-Alder reactions of diene (37)

General procedure: Equimolar quantities of **(37)** (3 mmol) and a dienophile were dissolved in benzene (10 ml) and the resulting solutions were refluxed for 1 hr to 9 days. The crude reaction mixtures were examined by 300 MHz nmr. The adducts either precipitated from the reaction mixture, were filtered, washed several times with benzene and recrystallised from suitable solvents or were purified by radial chromatography.

i) Reaction with methyl vinyl ketone **(63)** for 4 days gave 13-acetylheptacyclo[10,2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]-heptadec-15-ene-3,10-dione **(82)** which was recrystallised from benzene as colourless needles (0.33 g), m.p. 168-169°. ν_{max} 1730, 1710 cm^{-1}. ^{1}H n.m.r. δ_H 1.48, d,d,d, $J_{14b,1}$ 3.4Hz, $J_{14b,13}$ 5.9Hz, $J_{14b,14a}$ 12.7Hz, H14b; 1.79, br d, $J_{17b,17a}$ 11.5Hz, H17b; 1.96, br d, $J_{17a,17b}$ 11.5Hz, H17a; 2.10, methyl protons; 2.22, d,d,d, $J_{14a,1}$ 2.6Hz, $J_{14a,13}$ 10.3Hz, $J_{14a,14b}$ 12.7Hz, H14a; 2.63, m, H6,H7; 2.71 m, H4,H9; 2.75, m, H1; 2.86, m, H5,H8; 3.05, d,t, $J_{12,13}$ 1.7Hz, $J_{12,16}$ 1.7Hz, $J_{12,15}$ 6.7Hz, H12; 3.21, d,d,d, $J_{13,12}$ 1.7Hz, $J_{13,14a}$ 5.9Hz, $J_{13,14b}$ 10.3Hz, H13; 6.32, d,d,d, $J_{15,1}$ 1.5Hz, $J_{15,12}$ 6.7Hz, $J_{15,16}$ 8.5Hz, H15; 6.41, d,d,d, $J_{16,12}$ 1.7Hz, $J_{16,1}$ 6.9Hz, $J_{16,15}$ 8.5Hz, H16. ^{13}C n.m.r. δ_C 22.6, C14; 28.2, methyl carbon; 30.8, 32.4, (C1,C12); 40.8, C17; 41.8, 42.0 (C6,C7); 43.5, C5,C8; 45.1, C13; 54.0, C2,C11; 55.9, 56.0, (C4,C9); 131.5, 134.2, (C15,C16); 208.8, carbonyl; 212.7, 212.5 (C3,C10) (Found: $M^{+\cdot}$, 294.1250; C, 77.4; H, 6.4. $C_{19}H_{18}O_3$ requires: $M^{+\cdot}$, 294.1256; C, 77.5; H, 6.2%).

ii) Reaction with methyl acrylate **(64)** for 5 days gave 13-methoxycarbonylheptacyclo[10, 2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$] heptadec-15-ene-3,10-dione **(83)** which was recrystallised from dichloromethane-ethanol as colourless prisms (0.51 g), m.p. 151-153°. ν_{max} 1750, 1730 cm^{-1}. ^1H n.m.r. δ_H 1.59, d,d,d, $J_{14b,1}$ 3.3Hz, $J_{14b,13}$ 5.2Hz, $J_{14b,14a}$ 12.9 Hz, H14b; 1.79, br d, $J_{17b,17a}$ 10.8Hz, H17b; 1.96, br d, $J_{17a,17b}$ 10.8Hz, H17a; 2.25, d,d,d, $J_{14a,1}$ 2.6Hz, $J_{14a,13}$ 10.3Hz, $J_{14a,14b}$ 12.9 Hz, H14a; 2.63, m, H6,H7; 2.70, m, H4,H9; 2.75, m, H1; 2.85, m, H5,H8; 3.13, d,d,d, $J_{12,16}$ 0.9Hz, $J_{12,13}$ 2.1Hz, $J_{12,15}$ 6.0 Hz, H12; 3.19, d,d,d, $J_{13,12}$ 2.1Hz, $J_{13,14b}$ 5.2Hz, $J_{13,14a}$ 10.3Hz, H13; 3.64, s, methoxy protons; 6.35, m, H15; 6.47, m, H16. ^{13}C n.m.r δ_C 23.5, C14; 30.6, 33.0, (C1,C12); 36.5, C13; 40.8, C17; 41.7, 42.0, (C6,C7); 43.5, C5,C8; 51.8, methoxy carbon; 53.6, 53.8, (C2,C11); 55.8, 56.0, (C4,C9); 131.7, 134.8, (C15,C16); 175.4, ester carbonyl; 224.5, 227.8, (C3,C10) (Found: $M^{+}\cdot$; 310.1197; C 73.3; H, 5.7. $C_{19}H_{18}O_4$ requires: $M^{+}\cdot$; 310.1205; C, 73.5; H, 5.9%).

iii) Reaction with acrylic acid **(65)** for 7 days gave 3,10-dioxoheptacyclo[10,2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]heptadec-15-ene-13-carboxylic acid **(84)** which crystallised from the reaction mixture as colourless prisms (0.35 g), m.p. 276-278°. ν_{max} 3000, 1740, 1700 cm^{-1}. ^1H n.m.r. ($CDCl_3$/DMSO-d_6) δ_H 1.59, d,d,d, $J_{14b,1}$ 3.4Hz, $J_{14b,13}$ 4.7Hz, $J_{14b,14a}$ 13.3Hz, H14b; 1.80, br d, $J_{17b,17a}$ 11.4Hz, H17b; 1.95, br d, $J_{17a,17b}$ 11.4Hz, H17a; 2.19, d,d,d, $J_{14a,1}$ 2.4Hz, $J_{14a,13}$ 10.6Hz, $J_{14a,14b}$ 13.3Hz, H14a 2.64, m, H6,H7; 2.69, m, H4,H9; 2.73, m, H1; 2.86, m, H5,H8; 3.12, m, H12,H13; 6.37, m, H15; 6.46, m, H16. ^{13}C n.m.r. ($CDCl_3$/DMSO-d_6) δ_C 22.8, C14; 30.1, 32.5, (C1,C12); 35.8, C13;

40.2, C17; 41.1, 41.4, (C6,C7); 42.9, C5,C8, 53.1, 53.4, (C2,C11); 55.4, 55.5, (C4,C9); 131.4, 134.0, (C15,C16); 176.3, acid carbonyl; 220.7, 221.0, (C3,C10) (Found: $M^{+}\cdot$; 296.1050; C, 72.9; H, 5.5. $C_{18}H_{16}O_4$ requires: $M^{+}\cdot$; 296.1049; C, 73.0; H, 5.4%).

iv) Reaction with acrylonitrile **(66)** for 8 days gave 13-cyanoheptacyclo[10,2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]heptadec-15-ene-3,10-dione **(85)** which was recrystallised from dichloromethane-benzene as colourless prisms (0.46 g), m.p. 197-198°. ν_{max} 3000, 2250, 1740 cm^{-1}. ^{1}H n.m.r. δ_H 1.45, d,d,d, $J_{14b,1}$ 3.2Hz, $J_{14b,13}$ 4.9Hz, $J_{14b,14a}$ 13.6Hz, H14b; 1.81, br d, $J_{17b,17a}$ 11.3Hz, H17b; 1.97, br d, $J_{17a,17b}$ 11.3Hz, H17a; 2.45, d,d,d, $J_{14a,1}$ 2.2Hz, $J_{14a,13}$ 10.4Hz, $J_{14a,14b}$ 13.5Hz, H14a; 2.67, m, H6, H7; 2.72, m, H4,H9; 2.83, m, H1, 2.88, m, H5,H8; 3.04, d,t, $J_{12,16}$ 1.9Hz, $J_{12,13}$ 1.9Hz, $J_{12,15}$ 6.4Hz, H12; 3.33, d,d,d, $J_{13,12}$ 1.9Hz, $J_{13,14b}$ 4.9Hz, $J_{13,14a}$ 10.4Hz, H13; 6.53, m, H15; 6.65, m, H16. ^{13}C n.m.r. δ_C 22.0, C13; 25.2, C14; 29.9, 33.4, (C1,C12); 40.7, C17; 41.8, 42.6, (C6,C7); 43.5, 43.6, (C5,C8); 52.5, 52.8, (C2,C11); 55.7, 56.0, (C4,C9); 123.0, cyano carbon; 131.2, 135.9, (C15,C16); 211.4, 212.1, (C3,C10) (Found: $M^{+}\cdot$; 277.1104; C, 77.6; H, 5.4; N, 4.9. $C_{18}H_{15}NO_2$ requires: $M^{+}\cdot$; 277.1103; C, 78.0; H, 5.5; N, 5.1%).

v) Reaction with diethyl maleate **(68)** for 9 days gave 13,14-bis(ethoxycarbonyl)heptacyclo-[10,2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]heptadec-15-ene-3,10-dione **(86)** which was recrystallised from benzene as colourless prisms (0.21 g), m.p. 191-194°. ν_{max} 1735 cm^{-1}. ^{1}H n.m.r. δ_H 1.21, t, ^{3}J 7.2 Hz, methyl protons; 1.80, br d,

$J_{17b,17a}$ 11.3 Hz, H17b; 1.96, br d, $J_{17a,17b}$ 11.3 Hz, H17a; 2.67, m, H6,H7; 2.73, m, H4,H9; 2.87, m, H5,H8; 3.03, m, H1,H12, 3.53, br s, H13,H14; 4.04, m, methylene protons; 6.52, d,d, $J_{15,1}$ 3.3 Hz, $J_{15,12}$ 4.8 Hz, H15, H-6. ^{13}C n.m.r. δ_C 14.1, methyl carbons; 33.6, C1,C12; 40.7, C17; 41.5, 41.7, (C6,C7,C13,C14); 43.5, C5,C8; 53.3, C2,C11; 56.0, C4,C9; 60.5, methylene carbons; 132.2, C15,C16; 172.6, ester carbonyls; 212.0, C3,C10. (Found: $M^{+\cdot}$; 396.1562; C, 69.3; H, 6.2. $C_{23}H_{24}O_6$ requires: $M^{+\cdot}$; 396.1573; C, 69.7, H, 6.1%).

vi) Reaction with benzoquinone **(13a)** for 3 hr gave octacyclo[10,6,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$,$0^{13,18}$]heneicosa-15,19-diene-3,10,14,17-tetraone **(87)** (0.47 g) which crystallised from the reaction mixture as pale yellow needles, m.p. >240° (dec.) (lit.[97] 265-267°). ν_{max} 1745, 1720, 1675 cm^{-1}. ^1H n.m.r. δ_H 1.82, br d, $J_{21b,21a}$ 10.8Hz, H21b; 1.98, br d, $J_{21a,21b}$ 10.8Hz, H21a; 2.66, m, H6,H7; 2.76, m, H4,H9; 2.91, m, H5,H8; 3.48, m, H1,H12; 3.59, br s, H13,H18; 6.39, d,d, $J_{19,1}$ 3.1Hz, $J_{19,12}$ 4.6Hz, H19,H20; 6.66, s, H15,H16. ^{13}C n.m.r. δ_C 34.3, C1,C12, 40.7, C21; 41.7, C6,C7; 43.4, 43.5, (C5,C8,C13,C18); 53.2, C2,C11; 56.0, C4,C9; 133.8, C19,C20; 141.5, C15,C16; 197.8, C14,C17; 211.9, C3,C10 (Found: $M^{+\cdot}$; 332.1039. $C_{21}H_{16}O_4$ requires: $M^{+\cdot}$; 332.1049).

vii) Reaction with 2,3-dimethylbenzoquinone **(13b)**[141] for 24 hr gave 15,16-dimethyloctacyclo-[10,6,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$,$0^{13,18}$]heneicosa-15,19-diene-3,10,14,17-tetraone **(88)** (0.61 g) which crystallised from the reaction mixture as colourless prisms, m.p. 280-283°.

ν_{max} 1740, 1725, 1670 cm^{-1}. ^{1}H n.m.r. δ_H 1.83, br d, $J_{21b,21a}$ 10.8Hz, H21b; 1.94, s, methyl protons; 1.98, br d, $J_{21a,21b}$ 10.8Hz, H21a; 2.66, m, H6,H7; 2.75, m, H4,H9; 2.91; m, H5,H8; 3.54, m, H1,H12,H13,H18; 6.36, d,d, $J_{19,1}$ 3.0Hz, $J_{19,12}$ 4.2Hz, H19,H20. ^{13}C n.m.r. δ_C 13.4, methyl carbons; 33.7, C1,C12; 40.7, C21; 41.7, C6,C7; 43.2, 43.5, (C5,C8,C13,C18); 53.5, C2,C11; 56.1, C4,C9; 134.0, C19,C20; 147.0, C15,C16; 197.2, C14,C17; 212.2, C3,C10 (Found: $M^{+}\cdot$; 360.1361; C, 76.9; H, 5.6. $C_{23}H_{20}O_4$ requires: $M^{+}\cdot$; 360.1362; C, 76.7; H, 5.6%).

viii) Reaction with naphthoquinone (13e) for 24 hr gave nonacyclo[12,7,2,$2^{2,13}$,$0^{1,14}$,$0^{3,12}$,$0^{5,10}$,$0^{16,20}$,$0^{17,23}$,$0^{19,22}$]-pentacosa-5,7,9,24-tetraene-4,11,15,21-tetraone **(89)** (0.43 g) which crystallised from the reaction mixture as colourless prisms, m.p. 291-292°. ν_{max} 1740, 1695 cm^{-1}. ^{1}H n.m.r. δ_H 1.82, br d, $J_{18b,18a}$ 10.8Hz, H18b; 1.98, br d, $J_{18a,18b}$ 10.8Hz, H18a; 2.70, m, H22,H23; 2.77, m, H16,H20; 2.93, m, H17,H19; 3.68, m, H2,H13; 3.80, br s, H3,H12; 6.42, d,d, $J_{24,13}$ 3.3Hz, $J_{24,2}$ 4.5Hz, H24,H25; 7.69, d,d, $J_{7,9}$ 3.3Hz, $J_{7,6}$ 5.7Hz, H7,H8; 7.97, d,d, $J_{6,8}$ 3.3Hz, $J_{6,7}$ 5.7Hz, H6,H9. ^{13}C n.m.r. δ_C 34.2, C2,C13; 40.7, C18; 41.7, C22,C23; 43.6, C17,C19; 44.5, C3,C12; 53.4, C1,C14; 56.1, C16,C20; 126.7, C6,C9; 134.0, 134.4, (C7,C8,C24,C25); 135.7, C5,C10; 196.5, C4,C11; 212.1, C15,C21 (Found: $M^{+}\cdot$, 382.1186; C, 78.5; H, 5.1. $C_{25}H_{18}O_4$ requires: $M^{+}\cdot$; 382.1205; C, 78.5; H, 4.7%).

ix) Reaction with maleic anhydride (71) for 24 hr gave 5-oxaoctacyclo[10,5,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$,$0^{13,17}$]-eicosa-18-ene-3,10,14,16-tetraone **(90)** (0.73 g) which crystallised from the reaction mixture as colourless plates, m.p.

304-305° (lit.[78] 299-300°). ν_{max} 1870, 1840, 1790, 1740, 1725 cm^{-1}. ^1H n.m.r. δ_H 1.86, br d, $J_{20b,20a}$ 11.5Hz, H20b; 2.02, br d, $J_{20a,20b}$ 11.5Hz, H20a; 2.72, m, H6,H7; 2.79, m, H4,H9; 2.95, m, H5,H8; 3.36, br s, H1,H12; 3.77, m, H13,H17; 6.50, d,d, $J_{18,1}$ 3.0 Hz, $J_{18,12}$ 4.5 Hz, H18,H19. ^{13}C n.m.r. δ_C 32.6, C1,C12; 39.5, C13,C17, 40.8, C20; 41.6, C6,C7; 43.6, C5,C8; 52.8, C2,C8; 55.9, C4,C9; 132.9, C18,C19; 172.1, C14,C16; 211.0, C3,C10 (Found: $M^{+}\cdot$; 322.0847. $C_{19}H_{14}O_5$ requires: $M^{+}\cdot$; 322.0841).

x) Reaction with N-phenyl maleimide (72) for 1.5 hr gave 15-phenyl-15-azaoctacyclo-[10,5,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$,$0^{13,17}$]eicosa-18-ene-3,10,14,16-tetraone (91) (0.80 g) which crystallised from the reaction mixture as colourless plates, 344-345°. ν_{max} 1730 cm^{-1}. ^1H n.m.r. δ_H 1.85, br d, $J_{20b,20a}$ 11.3Hz, H20b; 2.01, br d, $J_{20a,20b}$ 11.3Hz, H20a; 2.72, m, H6,H7; 2.78, m, H4,H9; 2.94, m, H5,H8; 3.41, br s, H1,H12; 3.65, m, H13,H17; 6.46, d,d, $J_{18,1}$ 3.1 Hz, $J_{18,12}$ 4.6 Hz, H18,H19; 7.43, m, phenyls. ^{13}C n.m.r. δ_C 33.0, C1,C12; 38.8, C13,C17; 40.8, C20; 41.7, C6,C7; 43.5, C5,C8; 53.5, C2,C11, 55.9, C4,C9; 126.5, 128.6, 129.1, phenyl carbons; n.o. ipso phenyl carbon; 132.3, C18,C19; 177.3, C14,C16; 211.3, C3,C10 (Found: $M^{+}\cdot$; 397.1314; C, 75.6; H, 4.8; N, 3.5. $C_{25}H_{19}NO_4$ requires: $M^{+}\cdot$; 397.1314; C, 75.3; H, 4.6; N, 3.4%).

xi) Benzenediazonium-2-carboxylate prepared from anthranilic acid (0.67 g, 4.9 mmol) by the method of Crews and Beard[144] was allowed to decompose to benzyne (74) in the presence of (37) (1.1 g, 4.5 mmol) in dichloromethane (15 ml) by gentle heating on a steambath for 3 hr. The solvent was removed under reduced pressure to give an oil which was adsorbed onto silica on

a radial chromatograph. Elution with ether-petroleum ether (1:1) gave octacyclo[10,6,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$,$0^{13,18}$]-heneicosa-13,15,17,19-tetraene-3,10-dione **(95)** which was recrystallised from dichloromethane-benzene as colourless plates, 229-232° (dec.). ν_{max} 1735 cm^{-1}. ^1H n.m.r. δ_H 1.72, br d, $J_{21b,21a}$ 11.7Hz, H21b; 1.92, br d, $J_{21a,21b}$ 11.7Hz, H21a; 2.15, m, H6,H7; 2.65, m, H4,H9; 2.84, m, H5,H8; 3.91, d,d, $J_{1,19}$ 3.0Hz, $J_{1,20}$ 4.5Hz, H1,H12, 6.66, d,d, $J_{19,1}$ 3.0Hz, $J_{19,12}$ 4.5Hz, H19,H20; 7.16, d,d, 7.25, d,d, ^4J 3Hz, ^3J 6Hz, (H14,H15,H16,H17). ^{13}C n.m.r. δ_C 40.1, C1,C12; 40.4, C6,C7; 41.7, C17; 43.9, C5,C8; 54.7, C4,C9; 60.6, C2,C11; 124.4, 125.7, (C14,C15,C16,C17); 134.4, C19,C20; 141.9, C13,C18; 211.3, C3,C10 (Found: $M^{+\cdot}$; 300.1153. $C_{21}H_{16}O_2$ requires: $M^{+\cdot}$; 300.1150). Further elution gave octacyclo[10,6,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$,$0^{15,18}$]-heneicosa-13,15,17,19-tetraone-3,10-dione **(94)** which was recrystallised from dichloromethane-benzene as colourless prisms, 240-241°. ν_{max} 1740, 1730 cm^{-1}. ^1H n.m.r. δ_H 1.85, br d, $J_{21b,21a}$ 11.7Hz, H21b; 1.95, br d, $J_{21a,21b}$ 11.7Hz, H21a; 2.53, m, H4,H9; 2.74, m, H6,H7; 2.87, m, H5,H8; 3.96, d,d, $J_{1,19}$ 3.1Hz, $J_{1,20}$ 4.7Hz, H1,H12; 6.72, d,d, $J_{19,1}$ 3.1Hz, $J_{19,12}$ 4.7Hz, H19,H20; 7.07, d,d, 7.32, d,d, ^4J 2.7Hz, ^3J 5.6Hz, (H14,H15,H16,H17). ^{13}C n.m.r. δ_C 40.3, C1,C12; 40.4, C21; 41.3, C6,C7; 43.6, C5,C8; 54.8, C4,C9; 58.4, C2,C11; 125.2, 125.6, (C14,C15,C16,C17); 135.6, C19,C20; 140.8, C13,C18; 210.5, C3,C10) (Found: $M^{+\cdot}$; 300.1138; C, 83.8; H, 5.1. $C_{21}H_{18}O_2$ requires: $M^{+\cdot}$; 300.1150; C, 84.0; H, 5.4%).

xii) To a solution of **(37)** (0.45 g) in benzene (10 ml) was added freshly cracked cyclopentadiene **(75)** (1 ml). The mixture was refluxed at 85° for 7.5 hr after which time solvent was

removed under reduced pressure to give an oily residue which was absorbed onto silica on a radial chromatograph. Elution with ether-petroleum ether (1:1) gave heptacyclo[14,2,1,$1^{5,8}$,$0^{2,15}$,$0^{4,9}$,$0^{4,18}$,$0^{13,17}$]eicosa-6,10,12-triene-3,14-dione **(96)** (0.24 g) as reported by Mehta.[99] Further elution gave nonacyclo[18,2,1,$1^{5,8}$,$1^{13,16}$,$0^{2,19}$,$0^{4,9}$,$0^{4,22}$,$0^{12,17}$,$0^{17,21}$]-pentacosa-6,10,14-triene-3,18-dione **(97)** (0.19 g) which was recrystallised from benzene as colourless prisms, 144-145°. ν_{max} 1745 cm^{-1}. ^{1}H n.m.r. δ_H 1.11, br d, $J_{24b,24a}$ 8.7Hz, H24b,H25b; 1.67 br d, $J_{23b,23a}$ 11Hz, H23b; 1.72, br d, $J_{23a,23b}$ 11Hz, H23a; 1.95, m, (H21,H22,H24a,H25a); 2.85, m, H1,H2,H5,H8,H13,H16,H19,H20; 3.03, t, $J_{9,10}$ 4.1 Hz, H9,H12; 5.15, d, $J_{10,9}$ 4.1Hz, H10,H11; 6.20, d,d, ^{3}J 3.2Hz, $J_{6,7}$ 5.8Hz, 6.47, d,d, ^{3}J 2.5Hz, $J_{6,7}$ 5.8Hz, (H6,H7,H14,H15). ^{13}C n.m.r. δ_C 33.4, C23; 42.6, C9,C12; 43.5, C24,C25; 46.2, 47.1, 52.5, (C1,C5,C8,C13,C16,C20); 48.7, C21,C22; 55.3, C2,C19; 71.8, C4,C17, 133.9, C6,C15; 136.1, C10,C11; 141.3, C7,C14; 216.9, C3,C18 (Found: $M^{+}\cdot$; 356.1773; C, 84.4; H, 6.7. $C_{25}H_{24}O_2$ requires: $M^{+}\cdot$; 356.1776; C, 84.2; H, 6.8%).

xiii) A solution of **(37)** (0.27 g) and methyl propiolate **(77)** (0.4 ml) in benzene (5 ml) was heated under reflux for 9 days. The solvent was removed and and the residue was absorbed onto silica on a radial chromatograph and elution with ether gave unreacted **(37)** (0.11 g). Further elution gave 13-methoxycarbonyl-heptacyclo[10,2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]heptadeca-13,15-diene-3,10-dione **(99)** which was recrystallised from dichloromethane-ethanol as colourless prisms (0.10 g), 172-174°.

ν_{max} 1760, 1730 cm^{-1}. ^{1}H n.m.r. δ_H 1.89, br d, $J_{17b,17a}$ 11.1Hz, H17b; 1.98, br d, $J_{17a,17b}$ 11.1Hz, H17a; 2.61, m, H4,H6,H7,H9; 2.91, m, H5,H8; 3.72, m, H1; 3.74, s, methoxy protons; 4.18, d,t, $J_{12,14}$ 2.1Hz, $J_{12,16}$ 2.1Hz, $J_{12,15}$ 6.2Hz, H12; 6.50, m, H15; 6.63, m, H16; 7.43, d,d, ^{4}J 1.8Hz, $J_{14,1}$ 6.6Hz, H14. ^{13}C n.m.r. δ_C 36.9, 37.9, (C1,C12); 39.9, 40.0, (C6,C7); 41.7, C17; 44.0, C5,C8; 51.7, methoxy carbon; 54.2, C4,C9; 61.3, 61.9, (C2,C11); 133.7, C15, 135.2, C16; 139.0, C13; 144.6, C14; 164.6, ester carbonyl; 211.0, 211.1, (C3,C10) (Found: $M^{+}\cdot$; 308.1049; C, 73.9; H, 5.4. $C_{19}H_{16}O_4$ requires: $M^{+}\cdot$; 308.1049; C, 74.0; H, 5.2%).

xiv) A solution of **(37)** (0.5 g) and dimethyl acetylene-dicarboxylate **(78)** (0.28 ml) in benzene (5 ml) was heated under reflux for 1day. The solvent was removed to give a residue from which the major product 13,14-bis(methoxycarbonyl)-heptacyclo[10,2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]heptadec-13,15-diene-3,10-dione **(100)** was recrystallised from chloroform-benzene (0.25 g), m.p. 269-272° (lit.[79] 275-278°). ν_{max} 1760, 1745, 1715 cm^{-1}, ^{1}H n.m.r. δ_H 1.87, br d, $J_{17b,17a}$ 11.4Hz, H17b; 1.98, br d, $J_{17a,17b}$ 11.4Hz, H17a, 2.62, m, H6,H7; 2.65, m, H4,H9; 2.91, m, H5,H8; 3.79, s, methoxy protons; 4.06, d,d, $J_{1,15}$ 3.0Hz, $J_{1,16}$ 4.5 Hz, H1,H12; 6.65, d,d, $J_{15,1}$ 3.0Hz, $J_{15,12}$ 4.5Hz, H15,H16. ^{13}C n.m.r. δ_C 39.3, C1,C12; 40.1, C6,C7; 41.5, C17; 43.9, C5,C8; 52.3, methoxy carbons, 54.1, C4,C9; 60.4, C2,C11; 134.6, C15,C16; 143.1, C13,C14; 166.6, ester carbonyls; 209.8, C3,C10 (Found: $M^{+}\cdot$; 366.1086. $C_{21}H_{18}O_6$ requires: $M^{+}\cdot$; 366.1103). Crystals from the mother liquor were recrystallised several times to give 13,14-bis(methoxycarbonyl)heptacyclo-[10,2,2,$1^{5,8}$,$0^{2,6}$,$_{0}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]heptadec-13,15-diene-

3,10-dione (101) as colourless prisms from chloroform-benzene (0.18 g), m.p. 180-190° (lit.[99] 186-187°) ν_{max} 1760, 1745, 1710 cm^{-1}. ^{1}H n.m.r. δ_H 1.90, br d, $J_{17b,17a}$ 11.2Hz, H17b; 1.99, br d, $J_{17a,17b}$ 11.2Hz, H17a, 2.64, m, H4,H9; 2.75, m, H6,H7; 2.94, m, H5,H8; 3.82, s, methoxy carbons, 3.99, d,d, $J_{1,15}$ 2.9Hz, $J_{1,16}$ 4.3 Hz, H1,H12, 6.57, d,d, $J_{15,1}$ 2.9Hz, $J_{15,12}$ 4.3Hz, H15,H16. ^{13}C n.m.r. δ_C 39.0, C1,C12; 39.9, C6,C7; 41.7, C17; 44.0, C5,C8, 54.2, methoxy carbons; 60.3, C2,C11; 133.4, C15,C16; 142.4, C13,C14; 166.1, ester carbonyls, 210.1, C3,C10 (Found: $M^{+}\cdot$; 366.1100. $C_{21}H_{18}O_6$ requires: $M^{+}\cdot$; 366.1103).

xv) To a stirred solution of (37) (1.1 g) in benzene (15 ml) was added diethyl azodicarboxylate (79)[145] (0.8 ml) and the mixture was refluxed at 85-90° for 5 days. After removal of solvent the residue was absorbed onto silica on a radial chromatograph. Elution with ether gave 13,14-Bis(ethoxycarbonyl)-13,14-diazaheptacyclo[10,2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]heptadec-15-ene-3,10-dione (102) which was recrystallised from benzene-dichloromethane as colourless prisms (0.2 g), m.p. 212-213°. ν_{max} 3000, 1740, 1695 cm^{-1}. ^{1}H n.m.r. δ_H 1.3, m, methyl protons; 2.01, d, $J_{17b,17a}$ 11Hz, H17b; 2.08, d, $J_{17a,17b}$ 11Hz, H17a; 2.7; 3.0; 3.1; 3.3; 3.4; 4.25, methylene protons; 5.05; 5.2; 6.65. ^{13}C n.m.r. δ_C 14.4, 14.6, methyl carbons; 38.7; 38.8; 39.4; 39.5; 41.8; 44.1; 44.5; 48.9; 49.6; 51.4; 52.3; 54.6; 54.7; 62.4; 62.5; 63.1; 63.2; 130.2; 134.0; 134.1; n.o. ester carbonyls; 208.2, C3, C10 (Found: $M^{+}\cdot$; 398.1464; C, 63.4; H, 5.7; N, 7.3. $C_{21}H_{22}N_2O_6$ requires: $M^{+}\cdot$; 398.1478; C, 63.3; H, 5.6; N, 7.0%).

xvi) 1,4-Phthalazinedione **(80)** was prepared as follows[146]: to a stirred suspension of 1,4-phthalhydrazide (0.72 g, 4.50 mmol) in dichloromethane (50mL) was added N-bromosuccinamide (1.60 g, 9.00 mmol). After 5 min a solution of **(37)** (1.9 g, 4.46 mmol) in dichloromethane (5 ml) was added and the resulting solution was stirred for 5 hr at room temperature. The organic layer was washed successively with sodium thiosulphate solution (10%, 50 ml) and water (2 x 50 ml) dried over sodium sulphate and concentrated under reduced pressure to give a residue from which the major product 3,12-diazanonacyclo-[12,7,2,$2^{2,13}$,$0^{1,14}$,$0^{3,12}$,$0^{5,10}$,$0^{16,20}$,$0^{17,23}$,$0^{19,22}$]pentacosa-5,7,9,24-tetraene-4,11,15,21-tetraone **(104)** was recrystallised as a colourless powder (80 mg) from acetone, m.p. 295°. ν_{max} 1750, 1735, 1635 cm^{-1}. ^1H n.m.r. δ_H 1.94, br d, $J_{18b,18a}$ 11.5Hz, H18b; 2.07, $J_{18a,18b}$ 11.5Hz, H18a; 2.78, m, H16,H20; 3.00, m,H22,H23; 3.07, m, H17,H19; 6.09, d,d, $J_{2,25}$ 3.0 Hz, $J_{2,24}$ 4.5 Hz, H2,H13; 6.80, d,d, $J_{24,13}$ 3.0Hz, $J_{24,2}$ 4.5Hz, H24,H25; 7.85, d,d, $J_{7,9}$ 3.5Hz, $J_{7,6}$ 6.0 Hz, H7,H8; 8.36, d,d, $J_{6,8}$ 3.5Hz, $J_{6,7}$ 6.0Hz, H6,H9. ^{13}C n.m.r. δ_C 39.4, C22,C23, 41.7, C18; 44.3, C17,C19; 47.6, C2,C13; 54.8, C16,C20; 57.2, C1,C14; 127.6, C7,C8; 128.2, C5,C10; 131.5, C6,C9, 133.3, C24,C25; 154.6, C4, C10; 206.1, C15,C21 (Found: $M^{+\cdot}$; 384.1123. $C_{23}H_{16}N_2O_4$ requires: $M^{+\cdot}$; 384.1110). Crystals from the mother liquor were recrystallised several times from chloroform to give 3,12-diazanonacyclo-[12,7,2,$2^{2,13}$,$0^{1,14}$,$0^{3,12}$,$0^{5,10}$,$0^{16,20}$,$0^{17,23}$,$0^{19,22}$]pentacosa-5,7,9,24-tetraene-4,11,15,21-tetraone **(103)** as colourless needles (50 mg), m.p. >380° (dec.). ν_{max} 1760, 1740, 1640 cm^{-1}. ^1H n.m.r. δ_H 1.88, br d, $J_{18b,18a}$ 11.4Hz, H18b; 2.04, br d, $J_{18a,18b}$ 11.4Hz, H18a; 2.81, m, H16,H20; 2.88, m, H22,H23; 3.00, m, H17,H19; 6.19, d,d, $J_{2,25}$ 3.2Hz, $J_{2,24}$ 4.5 Hz, H2,H13; 6.84,

d,d, $J_{24,13}$ 3.2Hz, $J_{24,2}$ 4.5Hz, H24,H25; 7.77, d,d, $J_{7,9}$ 3.4Hz, $J_{7,6}$ 6.0Hz, H7,H8; 8.35, d,d, $J_{6,8}$ 3.4Hz, $J_{6,7}$ 6.0Hz, H6,H9. ^{13}C n.m.r. δ_C 40.1, C22,C23; 40.6, C18; 43.7, C17,C19, 46.5, C2,C13; 55.1, C16,C20; 127.7, C7,C8; 128.3, C5,C10; 131.8, C6,C9; 133.1, C24,C25; 204.0, C15,C21 (Found: $M^{+}\cdot$; 384.1121. $C_{23}H_{16}N_2O_4$ requires: $M^{+}\cdot$; 384.1110).

xvii) To a stirred ice-cooled solution of **(37)** (0.5 g) in dichloromethane (10 ml) was slowly added dropwise a solution of 4-phenyl-1,2,4-triazaoline-3,5-dione **(81)**[147] (0.39 g) in dichloromethane (15 ml) until a faint red colouration persisted. The solution was stirred for an additional 15 min and the solvent was removed to give a residue from which the major product 15-phenyl-13,15,17-triazaoctacyclo-[10,5,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$,$0^{13,17}$]eicos-18-ene-3,10,14,16-tetraone **(105)** which was recrystallised from benzene-chloroform as colourless prisms (90 mg), m.p. 300-301°. ν_{max} 1740, 1705, 1500, 1400, 1370 cm^{-1}. ^1H n.m.r. δ_H 1.88, br d, $J_{20b,20a}$ 11.9Hz, H20b; 2.07, br d, $J_{20a,20b}$ 11.9Hz, H20a; 2.78, m, H6,H7; 2.90, m, H4,H9; 2.98, m, H5,H8; 5.17, d,d, $J_{1,19}$ 2.7Hz, $J_{1,18}$ 4.6Hz, H1,H12; 6.69, d,d, $J_{18,12}$ 2.7Hz, $J_{18,1}$ 4.6Hz, H18,H19; 7.35, m, 7.43, m, phenyls. ^{13}C n.m.r. δ_C 39.8, C6,C7; 40.6, C20; 43.5, C5,C8; 49.6, C1,C12; 55.1, C4,C9; n.o. C2,C11; 125.6, 128.2, 129.1, 129.6, (phenyl carbons,C18,C19); n.o. ipso phenyl carbon; 155.6, C14,C16; 206.4, C3,C10 (Found: $M^{+}\cdot$; 399.1217. $C_{23}H_{19}N_3O_4$ requires: $M^{+}\cdot$; 399.1219). Crystals from the mother liquor were recrystallised several times to give 15-phenyl-13,15,17-triazaoctacyclo-[10,5,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$,$0^{13,17}$]eicos-18-ene-

3,10,14,16-tetraone **(106)** as colourless needles from benzene-chloroform (60 mg), m.p. 311-312°. ν_{max} 1740, 1710, 1405, 1375 cm^{-1}. ^1H n.m.r. δ_H 2.09, br d, $J_{20b,20a}$ 11.8Hz, H20b; 2.15, br d, $J_{20a,20b}$ 11.8Hz, H20a; 2.78, m, H4,H9; 3.10, m, H5,H8; 3.42, m, H6,H7; 5.04, d,d, $J_{1,19}$ 2.5Hz, $J_{1,18}$ 4.5Hz, H1,H12; 6.61, d,d, $J_{18,12}$ 2.5 Hz, $J_{18,1}$ 4.5 Hz, H18,H19; 7.39, m, 7.44, m, phenyls. ^{13}C n.m.r. δ_C 39.8, C6,C7; 42.0, C20; 44.3, C5,C8; 50.7, C1,C12; 54.9, C4,C9; 56.5, C2,C11; 125.5, 128.5, 129.2, phenyl carbons; 130.0, C18,C19; 131.2, ipso phenyl carbon; 156.1, C14,C16; 207.3, C3,C10 (Found: $M^{+}\cdot$; 399.1224, $C_{23}H_{17}N_3O_4$ requires: $M^{+}\cdot$; 399.1219).

Esterification of maleic anhydride adduct

To a solution of the adduct **(90)** in ethanol (50 ml) was added concentrated sulphuric acid (0.2 ml). The solution was refluxed at 80° for 24 hr. The reaction mixture was poured into a saturated solution of sodium carbonate (25 ml) and the aqueous phase was extracted with chloroform (2 x 25 ml). The organic extracts were washed, dried over anhydrous magnesium sulphate and concentrated under reduced pressure. The residue was absorbed onto silica on a radial chromatograph. Elution with ether gave 3-ethoxy-3-hydroxy-13,14-bis(ethoxycarbonyl)heptacyclo-[10,2,2,$1^{5,8}$,$0^{2,6}$,$0^{2,11}$,$0^{4,9}$,$0^{7,11}$]heptadeca-15-ene-10-one (0.15 g) **(93)** as colourless prisms from benzene, m.p. 98-100°. ν_{max} 3500, 3000, 1740 cm^{-1}. ^1H n.m.r. δ_H 1.19, m, (9H); 1.43, br d, $J_{17b,17a}$ 11.0Hz, H17b; 1.70, br d, $J_{17a,17b}$ 11.0Hz, H17a; 2.16, d,d,d, J 2.2Hz, J 5.5Hz, J 8.0Hz, (1H); 2.36, m, (2H); 2.51, m, (1H); 2.76, m, (1H); 2.99, m, (1H); 3.15, m, (H1,H12); 3.28, m, 3.45, m, (H13,H14); 3.73, m, (3H); 4.03, m, (3H); 6.34, br t, 6.57, br t, $J_{15,16}$ 7.3Hz, (H15,H16). ^{13}C n.m.r. δ_C 14.1,

14.6, 16.2, methyl carbons; 32.0; 36.9; 38.6; 39.6; 41.8; 42.2; 42.8; 44.3; 45.2; 50.4; 51.1; 55.3; 55.9; 58.1; 60.2; 61.0; 106.9, C10; 131.6, 133.8, (C15,C16); 173.0, 173.5, ester carbonyls; 213.3, C3 (Found: $M^{+}\cdot$; 442.1987. $C_{25}H_{30}O_7$ requires: $M^{+}\cdot$; 442.1991). Further elution gave the adduct **(86)** (0.30g) with identical physical and spectral properties to those described above.

Reduction of diketone **(37)**

To a stirred solution of (37) (5.0 g, 22.3 mmol) in dry methanol (30 ml) was slowly added portionwise sodium borohydride (1.75 g, 46.0 mmol). The reaction mixture was stirred for 5 hr after which time most of the methanol was removed under reduced pressure. The residue was diluted with water, extracted with ether (3 x 50 ml), dried over magnesium sulphate and the solvent removed under reduced pressure to give a colourless oil (4.5 g) which was recrystallised several times from carbon tetrachloride-acetone to give 3-endo,10-exo-dihydroxyhexacyclo-[10,2,1,$0^{2,11}$,$0^{4,9}$,$0^{4,14}$,$0^{9,13}$]pentadeca-5,7-diene **(111b)** which was recrystallised from acetone-carbon tetrachloride as colourless prisms (0.18 g), m.p. 187-190°. ν_{max} 3400, 2980, 2880 cm^{-1}. ^{1}H n.m.r. δ_H 1.14, d, $J_{15a,15b}$ 10.5Hz, H15a; 1.60, d, $J_{15b,15a}$ 10.5Hz, H15b; 2.38, m, (1H); 2.44, m, (2H); 2.70, m, (1H); 2.90, m, (2H); 3.68, m, H3; 4.99, m, H10; 5.32, br d, J 9.5Hz, H5 or H8; 5.72, br d, J 10.2Hz, H5 or H8; 5.82, d,d, J 5.4Hz, J 10.2Hz, H6 or H7; 5.91, d,d, J 5.4Hz, J 9.5Hz, H6 or H7. ^{13}C n.m.r. δ_C 32.9, C15; 42.6, 45.7, 46.2, 49.5, (C1,C12,C13,C14); 53.5, 54.3, (C2,C11); 74.2, 77.4, (C3,C10); 121.8, 124.7, 125.4, 126.7, (C5,C6,C7,C8) (Found: $M^{+}\cdot$, 228.1142;

C, 78.7; H, 6.9. $C_{15}H_{16}O_2$ requires: $M^{+}\cdot$, 228.1150; C, 78.9; H, 7.1%). The mother liquor gave 3-endo,10-endo-dihydroxyhexacyclo-[10,2,1,$0^{2,11}$,$0^{4,9}$,$0^{4,14}$,$0^{9,13}$]pentadeca-5,7-diene (111a) (3.5 g) as an oil. ν_{max} 3300, 3000 cm^{-1}. ^{1}H n.m.r. δ_H 0.92, d, $J_{15a,15b}$ 10.5Hz, H15a; 1.54, d, $J_{15b,15a}$ 10.5Hz, H15b; 2.41, m, 2.46, m, 2.79, m, (H1,H2,H11,H12,H13,H14); 3.58, m, H3,H10; 5.40, d,d, $J_{5,7}$ 2.6Hz, $J_{5,6}$ 7.9Hz, H5,H8; 5.88, d,d, $J_{6,8}$ 2.6Hz, $J_{6,5}$ 7.9Hz, H6,H7. ^{13}C n.m.r. δ_C 32.4, C15; 42.5, 45.8, (C1,C2,C11,C12); 47.4, C4,C9; 54.1, C2,C11; 75.9, C3,C10; 123.9, C5,C8; 128.0, C6,C7 (Found: $M^{+}\cdot$, 228.1151. $C_{15}H_{16}O_2$ requires: $M^{+}\cdot$, 228.1150). A sample of the latter diol (0.2g) was absorbed onto silica. Elution with chloroform gave 5,12-dihydroxytetracyclo[9,2,1,$1^{3,6}$,$0^{4,13}$]pentadeca-6(15),7,9,11(14)-tetraene (113) (50mg) which was recrystallised from acetone as a colourless powder, m.p. >250° (dec.). ν_{max} 3300, 2950 cm^{-1}. ^{1}H n.m.r. δ_H 0.66, d, 0.88, d, ^{2}J 8.2Hz, $(H2)_2$; 1.46, d, $J_{1,13}$ 8.5Hz, H1,H3; 2.34, br s, hydroxy protons; 3.38, d,d, $J_{4,5}$ 6.3Hz, $J_{4,3}$ 8.5Hz, H4,H13; 4.37, d, $J_{5,4}$ 6.3Hz, H5,H12; 5.55, t, J 1.8Hz, H14,H15; 6.40, d,d, 6.64, d,d, J 3.3Hz, J 5.7Hz, (H7,H8,H9,H10). ^{13}C n.m.r. δ_C 42.5, C1,C3; 47.7, C2; 48.2, C4,C13; 68.1, C5,C12; 120.3, 124.2, (C7,C8,C9,C10); 135.4, C14,C15; 139.3, C6,C11 (Found: $M^{+}\cdot$, 228.1185; C, 78.2; H, 7.1. $C_{15}H_{16}O_2$ requires: $M^{+}\cdot$, 228.1150; C, 78.9; H, 7.1%).

Reductions of ketones (8a-e,127) with cerium chloride/sodium borohydride reagent

General procedure: To a 0.4 M solutions of cerium(III)chloride in methanol at room temperature were added the diols (14) and mono-addition compound (127). Sodium

borohydride was then added portionwise to the stirred reaction mixtures. After the addition of sodium borohydride had been completed, the reaction mixtures were stirred for an additional 15 min and quenched with water. The resulting mixtures were extracted several times with ether and combined extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure.

i) Reaction of adduct **(8a)** (0.50 g, 2.88 mmol) with cerous chloride/methanol (5.76 mmol, 14 ml) and sodium borohydride (0.23 g, 6.05 mmol) as above gave endo-3,6-dihydroxytricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene **(14a)** (0.45 g) which was recrystallised from acetone as colourless needles, m.p.150° (lit.[148] 146-148°). ^{1}H n.m.r. δ_H 1.38, d, $J_{11b,11a}$ 8.0Hz, H11b; 1.43, d, $J_{11a,11b}$ 8.0Hz, H11a; 2.76, m, H2,H7; 3.01, m, H1,H8; 4.42, d,d, $J_{3,4}$ 1.3Hz, $J_{3,2}$ 7.2Hz, H3,H6; 5.67, d, $J_{4,3}$ 1.3Hz, H4,H5; 5.97, t, $J_{9,1}$ 1.9Hz, H9,H10;. ^{13}C n.m.r. δ_C 43.1, 45.0, (C1,C2,C7,C8); 50.4, C11; 66.3, C3,C6; 132.3, C9,C10; 134.9, C4,C5.

ii) Reaction of adduct **(8b)** (1.12 g, 5.6 mmol) with cerous chloride/methanol (11.2 mmol, 28 ml) and sodium borohydride (0.46 g, 12.2 mmol) as above gave endo-3,6-dihydroxy-4,5-dimethyltricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene **(14b)** which was recrystallised from acetone-benzene as colourless needles (0.40 g), m.p. 129-130°. ν_{max} 3300, 2980 cm^{-1}. ^{1}H n.m.r. δ_H 1.45, d, $J_{11b,11a}$ 7.9Hz, H11b; 1.51, d, $J_{11a,11b}$ 7.9Hz, H11b; 1.81, s, 4-Me,5-Me; 2.47, m, H2,H7; 2.85, m, H1,H8; 4.10, d, $J_{3,2}$ 4.6Hz, H3,H6; 6.19, t, $J_{9,1}$ 2.0Hz, H9,H10. ^{13}C n.m.r. δ_C 18.1, 4-Me,5-Me; 45.4, 45.6,

(C1,C2,C7,C8); 53.2, C11; 72.0, C3,C6; 133.6, C9,C10; 135.8, C4,C5 (Found: $M^{+\cdot}$, 206.1305; C, 75.4; H, 9.0. $C_{13}H_{18}O_2$ requires: $M^{+\cdot}$, 206.1307; C, 75.7; H, 8.8%).

iii) Reaction of adduct **(8c)** (0.35 g, 1.86 mmol) with cerous chloride/methanol (3.72 mmol, 9 ml) and sodium borohydride (0.16 g, 4.09 mmol) as above gave endo-3,6-dihydroxy-4-methyltricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene **(14c)** which was recrystallised from acetone-benzene as colourless prisms (0.17 g), m.p. 90-92°. ν_{max} 3400, 2950 cm^{-1}. ^1H n.m.r. δ_H 1.42, d, $J_{11b,11a}$ 8.0Hz, H11b; 1.47, d, $J_{11a,11b}$ 8.0Hz, H11a; 1.80, s, 4-Me; 2.60, m, H2,H7; 2.93, m, H1,H8; 4.16, d, $J_{3,2}$ 5.9Hz, H3; 4.35, t, $J_{6,7}$ 5.2Hz, H6; 5.63, m, H5; 6.09, m, H9,H10. ^{13}C n.m.r. δ_C 20.3, 4-Me; 44.7, 44.8, 45.1, 45.3, (C1,C2,C7,C8); 51.9, C11; 66.1, C6; 69.9, C3; 127.6, C5; 133.5, C9,C10; 142.5, C4 (Found: $M^{+\cdot}$, 192.1153; C, 75.2; H, 8.1. $C_{12}H_{16}O_2$ requires: $M^{+\cdot}$, 192.1150; C, 75.0; H, 8.4%).

iv) Reaction of adduct **(8d)** (0.75 g, 3.26 mmol) with cerous chloride/methanol (6.52 mmol, 16 ml) and sodium borohydride (0.46 g, 12.2 mmol) as above gave a residue which was absorbed onto silica on a radial chromatograph. Elution with ether-petroleum ether (1:1) gave endo-4-t-butyl-3,6-dihydroxytricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene **(14d)** (0.21 g) which was recrystallised from benzene as colourless needles, m.p. 122°. ν_{max} 3300, 2980 cm^{-1}. ^1H n.m.r. δ_H 1.13, Bu^t; 1.49, d, $J_{11b,11a}$ 8.0Hz, H11b; 1.54, d, $J_{11a,11b}$ 8.0Hz, H11a; 2.86, m, H2,H7; 4.34, m, H6; 4.41, m, H3; 6.06, d, $J_{5,6}$ 5.5Hz, H5; 6.24, t, $J_{9,1}$ 1.9Hz, H9,H10. ^{13}C n.m.r. δ_C 28.5, Bu^t; 35.9, C_q (Bu); 45.3, 45.7, 45.9, 47.4,

(C1,C2,C7,C8); 53.8, C11; 65.7, 65.9, (C3,C6); 125.5, C5; 133.5, 133.9, (C9,C10); 159.2, C4 (Found: $M^{+}\cdot$ - H_2O, 216.1519; C, 77.1; H, 9.5. $C_{15}H_{22}O_2$ requires: $M^{+}\cdot$ - H_2O, 216.1514; C, 76.9; H, 9.5%). Further elution gave endo-4-t-butyl-6-hydroxytricyclo[6,2,1,$0^{2,7}$]undeca-4,9-diene-3-one **(115a)** (0.21 g) as an oil or semi-crystalline solid. ν_{max} 3500, 3000, 1740 cm^{-1}. ^1H n.m.r. δ_H 1.10, Bu^t; 1.32, d, $J_{11b,11a}$ 8.4Hz, H11b; 1.42, d, $J_{11a,11b}$ 8.4Hz, H11a; 2.92, d,d,d, $J_{7,8}$ 3.6Hz, $J_{7,2}$ 9.3Hz, $J_{7,6}$ 9.3Hz, H7; 3.03, d,d, $J_{2,1}$ 4.1Hz, $J_{2,7}$ 9.3Hz, H2; 3.18, m, H1; 3.32, m, H8; 4.74, d,d, $J_{6,5}$ 2.4Hz, $J_{6,7}$ 9.3Hz, H6; 5.77, d,d, $J_{10,8}$ 3.0Hz, $J_{10,9}$ 5.6Hz, H10; 6.14, d,d, $J_{9,1}$ 2.8Hz, $J_{9,10}$ 5.6Hz, H9; 6.26, d, $J_{5,6}$ 2.4Hz, H5. ^{13}C n.m.r. δ_C 29.0, ^tBu; 34.5, C_q (Bu); 40.4, 45.6, 49.3, 50.2, 51.1, (C1,C2,C7,C8,C11); 66.0, C6; 135.0, C9,C10; 143.4, C5; 146.9, C4; 200.5, C3 (Found: $M^{+}\cdot$, 232.1468. $C_{15}H_{20}O_2$ requires: $M^{+}\cdot$, 232.1463).

v) Reaction of adduct **(8e)** (3.0 g, 13.2 mmol) with cerous chloride/methanol (26.4 mmol, 66 ml) and sodium borohydride (1.02 g, 26.8 mmol) as above gave endo-3,10-dihydroxytetracyclo[6,2,1,$0^{2,7}$]pentadeca-4,6,8,13-tetraene **(14e)** (2.4 g) which was recrystallised from acetone as colourless prisms, m.p. 158-159°. ν_{max} 3350, 2950, 1715 cm^{-1}. ^1H n.m.r. δ_H 1.42, d, $J_{15b,15a}$ 8.1Hz, H15b; 1.46, d, $J_{15a,15b}$ 8.1Hz, H15a; 2.82, d,d, $J_{2,1}$ 2.1Hz, $J_{2,3}$ 3.5Hz, H2,H11; 3.00, m, H1,H12; 4.88, d,d, $J_{3,5}$ 2.1Hz, $J_{3,2}$ 3.5Hz, H3,H10; 5.77, m, H13,H14; 7.29, m, H5,H6,H7,H8. ^{13}C n.m.r. δ_C 45.1, 45.6, (C1,C2,C11,C12); 51.9, C15; 70.3, C3,C10; 125.1, 127.6, (C5,C6,C7,C8); 133.7, C13,C14; 139.4, C4,C9 (Found: $M^{+}\cdot$,

228.1151; C, 77.0; H, 7.3. $C_{15}H_{16}O_2$ requires: $M^{+\cdot}$, 228.1150; C, 78.9; H, 7.0%).

vi) Reaction of the mono-addition compound **(127)** (0.33 g, 1.1 mmol) with cerous chloride/methanol (1.1 mmol, 3 ml) and an excess sodium borohydride (0.06 g, 1.6 mmol) as above gave endo-3,10-dihydroxy-3-phenyltetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]-pentadeca-4,6,8,13-tetraene **(128)** which was recrystallised as colourless prisms from chloroform (0.15 g), m.p. 174-174.5°. ν_{max} 3250, 2970 cm^{-1}. ^1H n.m.r. δ_H 1.40, t, ^3J 1.7Hz, H15a,H15b; 2.84, m, 3.06, m, (H1,H12); 2.89, d,d,d, $J_{11,12}$ 3.6Hz, $J_{11,10}$ 6.3Hz, $J_{11,2}$ 10.4Hz, H11; 3.23, d,d, $J_{2,1}$ 3.4Hz, $J_{2,11}$ 1-.4Hz, H2; 4.78, d, $J_{10,11}$ 6.3Hz, H10; 5.72, m, 5.78, m, (H13,H14); 7.2-7.5, m, phenyls. ^{13}C n.m.r. δ_C 44.9, 45.2, 45.5, 51.2, 51.7, (C1,C2,C11,C12,C15); 70.1, C10; n.o., C3; 125.1, 125.3, 126.6 (2C), 127.0, 127.3, 127.4, 127.9 (2C), (phenyl carbons,C5,C6,C7,C8); 133.4, 133.5, (C13,C14); 140.1, 142.1, 145.3, (ipso phenyl carbon,C4,C9) (Found: $M^{+\cdot} - H_2O$, 286.1377; C, 82.6; H, 6.4. $C_{21}H_{20}O_2$ requires: $M^{+\cdot} - H_2O$, 286.1358; C, 82.9; H, 6.6%)

Dehydration of diol **(14e)**

To a solution of diol **(14e)** (0.70 g,3.07 mmol) in dry pyridine (5 ml) was added p-toluenesulphonyl chloride (1.76 g, 9.21 mmol) and the mixture was stirred at 0° for 5 days. The crude reaction mixture was poured into water (50 ml) and the resulting solution extracted with dichloromethane (5 x 30 ml). The organic extracts were washed with water (2 x 50 ml) and brine (50 ml) and the solvent was removed under reduced pressure to

give a residue which was absorbed onto silica on a radial chromatograph. Elution with dichloromethane-petroleum ether (3:7) gave tetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]pentadeca-2,4,6,8,10-pentaene **(15e)** which was recrystalised as colourless prisms from acetone-ethanol (0.13 g), m.p. 81-81.5°. ν_{max} 2950, 1280, 880, 740, 700 cm^{-1}. ^{1}H n.m.r. δ_H 2.23, d, $J_{15b,15a}$ 7.5Hz, H15b; 2.35, d, $J_{15a,15b}$ 7.5Hz, H15a; 3.96, m, H1,H12; 6.73, t, $J_{13,1}$ 2.2Hz, H13,H14; 7.37, d,d, $J_{6,8}$ 3.2Hz, $J_{6,5}$ 5.9Hz, H6,H7; 7.56, s, H3,H10; 7.69, d,d, $J_{5,7}$ 3.2Hz, $J_{5,6}$ 5.9Hz, H5,H8. ^{13}C n.m.r. δ_C 49.5, C15; 66.4, C1,C12; 119.1, C6,C7; 124.9, C13,C14; 131.8, C4,C9; 141.8, C3,C10; 148.2, C2,C11 (Found: $M^{+}\cdot$, 192.0939; C, 93.6; H, 6.2. $C_{15}H_{12}$ requires: $M^{+}\cdot$, 192.0939; C, 93.7; H, 6.3%).

Reactions of adducts **(8a,e)** with methyl magnesium iodide

General procedure: A three-necked round-bottomed flask (100 ml) fitted with a pressure-equalised dropping funnel and a condenser with drying-tube (calcium chloride) was charged with magnesium turnings in ether (20 ml). Excess methyl iodide in ether (10 ml) was slowly added dropwise and the resulting Grignard reagent was refluxed at 40° for 30 min and then the diketone in ether (20 ml) was added dropwise over a 15 min period. The reaction mixture was stirred at 40° for 3 hr. The crude reaction mixtures were poured carefully into saturated ammonium chloride solution (100 ml) and the aqueous phase extracted several times with ether. The combined extracts were dried (sodium sulphate) and concentrated under reduced pressure. The crude products were absorbed onto silica on a radial chromatograph.

i) The reaction of adduct **(8a)** (1.0 g, 5.75 mmol) with methyl magnesium iodide required magnesium turnings (1.38 g, 57.5 mmol) and methyl iodide (4 ml) was performed as above. Following workup the residue was recrystallised from ethanol-dichloromethane to give endo-3,6-dihydroxy-3,4,6-trimethyltricyclo[6,2,1,$0^{2,7}$]undec-9-ene **(117)** as colourless prisms (15 mg), m.p. 168-169°. ν_{max} 3250, 2950 cm^{-1}. ^1H n.m.r. δ_H 0.97, d, ^3J 6.8Hz, 4-Me; 1.26, s, 1.27, s, (3-Me,6-Me); 1.31, d, $J_{11b,11a}$ 8.0Hz, H11b; 1.34, d,d, $J_{5a,4}$ 6.6Hz, $J_{5a,5b}$ 15.0Hz, H5a; 1.44, d, $J_{11a,11b}$ 8.0Hz, H11a; 1.60, m, H4; 1.90, d,d, $J_{5b,4}$ 10.5Hz, $J_{5b,5a}$ 15.0Hz, H5b; 2.19, d,d, 2.27, d,d, $J_{2,1}$ 3.1Hz, $J_{2,7}$ 11.3Hz, $J_{7,8}$ 3.1Hz, $J_{7,2}$ 11.3Hz, (H2,H7); 3.00, m, H1,H8; 6.21, m, H9,H10. ^{13}C n.m.r. δ_C 16.5, 4-Me; 27.4, 31.2, (3-Me,6Me); 37.2; 44.5, 44.8, 45.0, (C1,C5,C8); 50.1, 52.5 (2C), (C2,C7,C11); 70.8, 71.8, (C3,C6); 134.1, 134.7, (C9,C10) (Found: $M^{+}\cdot$, 222.1630; C, 75.7; H, 9.9. $C_{14}H_{22}O_2$ requires: $M^{+}\cdot$, 222.1620; C, 75.6; H, 10.0%). The remainder of the residue was absorbed onto silica. Elution with ether-petroleum ether (1:1) gave endo-3-hydroxy-3,4-dimethyltricyclo-6,2,1,$0^{2,7}$]undec-9-ene-6-one **(116a)** (0.32 g) which was recrystallised from hexane-dichloromethane as colourless prisms, m.p. 70-72°. ν_{max} 3400, 3000, 1700 cm^{-1}. ^1H n.m.r. δ_H 0.95, d, ^3J 6.4Hz, 5-Me; 1.33, s, 6-Me; 1.34, br d, $J_{11b,11a}$ 8.3Hz, H11b; 1.51, br d, $J_{11a,11b}$ 8.3Hz, H11a; 1.91, d,d, $J_{4a,5}$ 11.1Hz, $J_{4a,4b}$ 17.7Hz, H4a; 2.03, m, H5; 2.32, d,d, $J_{4b,5}$ 6.2Hz, $J_{4b,4a}$ 17.7Hz, H4b; 2.66, d,d, $J_{7,8}$ 3.2Hz, $J_{7,2}$ 11.4Hz, H7; 2.96, d,d, $J_{2,1}$ 3.8Hz, $J_{2,7}$ 11.4Hz, H2; 3.03, m, H8; 3.23, m, H1; 6.18, d,d, $J_{9,8}$ 3.0Hz, $J_{9,10}$ 5.8Hz, H9; 6.34 d,d, $J_{10,8}$ 3.1Hz, $J_{10,9}$ 5.8Hz, H10. ^{13}C n.m.r. δ_C 14.5, 5-Me; 26.1, 6-Me; 38.1, C5; 43.7, C4,C8; 43.9,

C1; 50.4, C11; 52.6, C7; 53.2, C2; 71.9, C6; 133.0, C9; 138.3, C10; 212.9, C3 (Found: $M^{+}\cdot$, 206.1304; C, 75.5;-H, 9.0. $C_{13}H_{18}O_2$ requires: $M^{+}\cdot$, 206.1307; C, 75.7; H, 8.8%). Further elution gave

endo-3-hydroxy-3,4-dimethyltricyclo[6,2,1,$0^{2,7}$]undec-9-ene-6-one **(116b)** (0.24 g) which was recrystallised from hexane-dichloromethane as colourless prisms, m.p. 72.5-74°. ν_{max} 3400, 2950, 1680 cm^{-1}. ^{1}H n.m.r. δ_H 1.09, d, ^{3}J 7.2Hz, 5-Me; 1.34, br d, $J_{11b,11a}$ 8.4Hz, H11b; 1.35, s, 6-Me; 1.49, br d, $J_{11a,11b}$ 8.4Hz, H11a; 1.90, d,d, $J_{4a,5}$ 4.5Hz, $J_{4a,4b}$ 18.5Hz, H4a; 2.03, m, H5; 2.44, d,d, $J_{4b,5}$ 6.9Hz, $J_{4b,4a}$ 18.5Hz, H4b; 2.71, d,d, $J_{7,8}$ 3.2Hz, $J_{7,2}$ 10.8Hz, H7; 2.89, d,d, $J_{2,1}$ 3.9Hz, $J_{2,7}$ 10.8Hz, H2; 3.07, m, H8; 3.26, m, H1; 6.23, d,d, $J_{9,1}$ 2.7Hz, $J_{9,10}$ 5.7Hz, H9; 6.29, d,d, J0,8 3.0Hz, $J_{10,9}$ 5.7Hz, H10. ^{13}C n.m.r δ_C 17.1, 5-Me; 26.4, 6-Me; 38.0, C5; 44.1, C4; 44.6, C8; 45.3, C1; 49.2, C7; 50.6, C11; 51.5, C2; 73.3, C6; 134.2, C9; 137.6, C10; 213.0, C3 (Found: $M^{+}\cdot$, 206.1315; C, 75.6; H, 8.8. $C_{13}H_{18}O_2$ requires: $M^{+}\cdot$, 206.1307; C, 75.7; H, 8.8%).

ii) The reaction of adduct **(8e)** (1.0 g, 4.46 mmol) with methyl magnesium iodide required magnesium turnings (1.07 g, 44.6 mmol) and methyl iodide (4ml) and was performed as above. Following workup the residue was recrystallised from chloroform to give

endo-3,10-dihydroxy-3,10-dimethyltetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]-pentadeca-4,6,8,13-tetraene **(123b)** as colourless prisms (60 mg), m.p. 224°. ν_{max} 3250, 3000 cm^{-1}. ^{1}H n.m.r. δ_H 1.42, d, $J_{15b,15a}$ 8.1Hz, H15b; 1.56, d, $J_{15a,15b}$ 8.1Hz, H15a; 1.76, s, 3-Me,10-Me; 2.44, t, $J_{2,1}$ 1.6Hz, H2,H11; 3.11, m, H1,H12; 6.27, t, $J_{13,1}$ 1.9Hz, H13,H14; 7.31, d,d, $J_{6,8}$ 3.4Hz, $J_{6,5}$ 5.7Hz,

H6,H7; 7.55, d,d, $J_{5,7}$ 3.4Hz, $J_{5,6}$ 5.7Hz, H5,H8. ^{13}C n.m.r. δ_C 27.0, 3-Me,10-Me; 44.8, C1,C12; 51.3, C2,C11; 52.4, C15; 71.1, C3,C10; 124.2, 127.6, (C5,C6,C7,C8); 133.7, C13,C14; 143.7, C4,C9 (Found: $M^{+}\cdot$, 256.1444; C, 79.2; H, 7.9. $C_{17}H_{20}O_2$ requires: $M^{+}\cdot$, 256.1463; C, 79.7; H, 7.9%). The remainder of the residue was absorbed onto silica on a radial chromatograph and elution with ether-petroleum ether (1:9) gave 3,10-dimethyl-11-oxatetracyclo[8,6,0,$0^{4,9}$,$0^{12,16}$]hexadeca-2,4,6,8,13-pentaene as an oil (125) (0.22 g), ν_{max} (smear) 2950, 1090, 1020, 765 cm^{-1}. ^1H n.m.r. δ_H 1.37,br s, 10-Me; 1.90, d,d,d,d, $J_{15b,14}$ 2.3Hz, $J_{15b,13}$ 2.3Hz, $J_{15b,16}$ 4.4Hz, $J_{15b,15a}$ 17.9Hz, H15b; 2.02, d,d,d,d, $J_{15a,14}$ 2.3Hz, $J_{15a,13}$ 2.3Hz, $J_{15a,16}$ 9.4Hz, $J_{15a,15b}$ 17.9Hz, H15a; 2.12, d, $J_{3\text{-}Me,2}$ 3.0Hz, 3-Me; 2.77, d,d,d, $J_{1,10\text{-}Me}$ 1.1Hz, $J_{1,2}$ 6.5Hz, $J_{1,16}$ 9.4Hz, H1; 3.07, d,d,d,d, $J_{16,15b}$ 4.4Hz, $J_{16,12}$ 7.5Hz, $J_{16,15a}$ 9.4Hz, $J_{16,1}$ 9.4Hz, H16; 5.23, d,d,d, $J_{12,14}$ 2.3Hz, $J_{12,13}$ 4.5Hz, $J_{12,16}$ 7.5Hz, H12; 5.31, d,d,d,d, $J_{14,12}$ 2.3Hz, $J_{14,15a}$ 2.3Hz, $J_{14,15b}$ 2.3Hz, $J_{14,13}$ 5.7Hz, H14; 5.44, d,d,d,d, $J_{13,15a}$ 2.3Hz, $J_{13,15b}$ 2.3Hz, $J_{13,12}$ 4.5Hz, $J_{13,14}$ 5.7Hz, H13; 5.80, d,d,d, $J_{2,5}$ 1.8Hz, $J_{2,3\text{-}Me}$ 3.0Hz, $J_{2,1}$ 6.5Hz, H2; 7.15, m, H5,H6,H7; 7.42, m, H8. ^{13}C n.m.r. δ_C 19.5, 3-Me; 30.4, 10-Me; 34.1, C15; 44.9, C16; 48.6, C1; 82.1, C10; 88.0, C12; 122.2, 126.4, 127.1, (C5,C6,C7); 123.9, C2; 125.7, C8; 129.8, C13; 132.9, 133.0, (C3,C4); 134.4, C14; 141.7, C9 (Found: $M^{+}\cdot$, 238.1366. $C_{17}H_{18}O$ requires: $M^{+}\cdot$, 238.1358). Further elution gave 3,10-dihydroxytetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]pentadeca-2,4,6,8,10-pentaene (122) (10 mg), ν_{max} 3300, 1660, 1600 cm^{-1} (lit.[149] 3280, 1645, 1605 cm^{-1}). Elution with ether-petroleum ether (1:1) gave <u>endo</u>-3,10-dihydroxy-3,10-dimethyltetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]-

pentadeca-4,6,8,13-tetraene (123a) (0.55 g) as an oil or semi-crystalline solid. ν_{max} 3400, 3000 cm^{-1}. ^1H n.m.r. δ_H 1.27, br d, $J_{15a,15b}$ 8.0Hz, H15a; 1.37, d, $J_{15b,15a}$ 8.0Hz, H15b; 1.72, s, 1.76, s, (3-Me,10Me); 2.82, d,d, 2.93, d,d, $J_{2,1}$ 3.6Hz, $J_{2,11}$ 9.3Hz, $J_{11,12}$ 3.6Hz, $J_{11,2}$ 9.3Hz, (H2,H11); 2.94, m, 3.08, m, (H1,H12); 5.22, d,d, 5.40, d,d, $J_{13,1}$ 2.9Hz, $J_{13,14}$ 5.6Hz, $J_{14,12}$ 2.9Hz, $J_{14,13}$ 5.6Hz, (H13,H14); 7.24, m, (3H), 7.59, d,d, ^4J 1.5Hz, ^3J 7.5Hz, (1H), phenyls. ^{13}C n.m.r. δ_C 28.2, 36.0, (3-Me,10-Me); 46.6, 46.9, 48.7, 50.1, 50.3, (C1,C2,C11,C12,C15); 71.0, 72.6 (C3,C10); 122.8, 123.9, 126.4, 128.1, (C5,C6,C7,C8); 132.9, 133.8, (C13,C14); 139.2, 144.9, (C4,C9) (Found: $M^{+\cdot}$, 256.1477. $C_{17}H_{20}O_2$ requires: $M^{+\cdot}$, 256.1463). Further elution gave endo-3-hydroxy-3-methyltetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]pentadeca-4,6,8,13-tetraene-10-one (124) (70mg) as an oil or semi-crystalline solid. ν_{max} 3450, 3000, 1670 cm^{-1}. ^1H n.m.r. δ_H 1.43, s, 10-Me; 1.45, t, J 1.6Hz, H15a,H15b; 1.88, hydroxy proton; 2.93, d,d, J 3.4Hz, $J_{2,11}$ 8.4Hz, H2 or H11; 3.27, m, (H1,H12,H2 or H11); 5.43, d,d, 5.58, d,d, J 2.6Hz, J 2.9Hz, $J_{13,14}$ 5.6Hz; 7.27, m, H8; 7.57, m, (H5,H6,H7). ^{13}C n.m.r. δ_C 37.8, 10-Me; 46.1, 49.9, 50.0, 50.1, 51.3, (C1,C2,C11,C12,C15); 71.6, C10; 123.4, 125.7, 126.9, 133.7, 133.9, 134.4, (C5,C6,C7,C8,C13,C14); 133.6, C4; 148.2, C9; 200.8 C3. (Found: $M^{+\cdot}$, 240.1155. $C_{16}H_{16}O_2$ requires: $M^{+\cdot}$, 240.1150).

Cyclisation of (117) to ethers (118)

An nmr sample of (117) in deuteriochloroform isomerised to the cyclic ethers (118) over a period of 3 days but these compounds were not further purified but ^{13}C and incomplete ^1H nm data is given for the major isomer. ^1H n.m.r δ_H 1.0, 3H; 1.15,

3H; 1.2, 3H; 3.05, 1H; 4.2, 1H. ^{13}C n.m.r. δ_C 13.8; 27.2; 28.6; 35.5; 37.7; 38.6; 38.8; 38.9; 45.8; 48.3; 49.9; 72.6; 78.0; 79.0.

Reaction of diol **(123a)** with ethanol

Recrystallisation of the diol **(123a)** (0.2 g) from ethanol gave a residue which was absorbed onto silica on a radial chromatograph. Elution with ether-petroleum ether (1:3) gave 2-hydroxy-2,5-dimethyl-3-(2-ethoxycyclopent-3-enyl)bicyclo[4,4,0] deca-4,6,8,10-tetraene **(126)** (65 mg) which was recrystallised from hexane-dichloromethane as colourless prisms, m.p. 97-98°. ν_{max} 3450, 3000 cm^{-1}. ^1H n.m.r. δ_H 0.98, t, ^3J 7.0Hz, 3H, methyl protons; 1.44, s, 2-Me; 1.98, d,d, ^3J 7.0Hz, ^2J 15.4Hz, 1H, methylene proton; 2.09. d, $J_{5\text{-Me},4}$ 1.3Hz, 5-Me; 2.26, d,d, $J_{5b',1}$ 4.4Hz, $J_{5b',5a'}$ 16.1Hz, H5b'; 2.38, d,d, $J_{5a',1}$ 9.2Hz, $J_{5a',5b'}$ 16.1Hz, H5a'; 2.64, d,d, $J_{3,4}$ 5.6Hz, $J_{3,1'}$ 9.2Hz, H3; 2.75, d,d,d,d, $J_{1',5b'}$ 4.4Hz, $J_{1',2'}$ 7.6Hz, $J_{1',5a'}$ 9.2Hz, $J_{1',3}$ 9.2Hz, H1'; 3.07, d,d, ^3J 7.0Hz, ^2J 15.4Hz, 1H, methylene proton; 3.67, br d, $J_{2',1'}$ 7.6Hz, H2'; 4.13, br s, hydroxy proton; 5.68, d,d, $J_{4,5\text{-Me}}$ 1.3Hz, $J_{4,3}$ 5.6Hz, H4; 5.85, m, H3',H4'; 7.20, m, 7.30, m, (H7,H8,H9); 7.75, m, H10. ^{13}C n.m.r. δ_C 15.3, OCH_2CH_3; 19.8, 5-Me; 31.5, 2-Me; 33.7, C5'; 45.6, C1',C3; 64.1, OCH_2; 73.0, C2; 84.3, C2'; 122.6, 124.2, 124.6, 126.5, 127.7, 129.9, 133.2, (C4,C7,C8,C9,C10,C3',C4'); 132.2, 133.7, 144.2, (C1,C5,C6) (Found: C, 80.1; H, 8.5. $C_{19}H_{24}O_2$ requires: C, 80.2; H, 8.5%).

Reaction of adducts **(8a,e)** with phenyl magnesium bromide

General procedure: To a suspension of a slight excess of magnesium turnings in ether (20 ml) was added a crystal of iodine and approximately one quarter of the required bromobenzene. A

glass rod was used to induce the reaction and the balance of the bromobenzene in ether (10 ml) was added over a period of 15 min. The resulting Grignard reagent was refluxed for 30 min and the diketone in ether (20 ml) was then added over a 20 min period. The reaction mixture was stirred at 40° for 4 hr. Workup of the crude reaction mixture followed as above. The crude products were absorbed onto silica on a radial chromatograph.

i) The reaction of adduct **(8a)** (1.0 g, 5.75 mmol) with phenyl magnesium bromide required magnesium turnings (1.52 g, 63.3 mmol) and bromobenzene (6.1 ml, 57.5 mmol) was performed as above. Following workup and absorption of the crude reaction mixture onto silica, elution with petroleum ether gave biphenyl (0.24 g). Elution with ether-petroleum ether (1:1) gave endo-4-phenyltricyclo[6,2,1,$0^{2,7}$]undec-9-ene-3,6-dione **(119)** (0.31 g) which was recrystallised from ethanol-dichloromethane as colourless needles, m.p. 152-153°. ν_{max} 3025, 1715, 1700 cm^{-1}. ^1H n.m.r. δ_H 1.23, d, $J_{11b,11a}$ 8.6Hz, H11b; 1.41, br d, $J_{11a,11b}$ 8.6Hz, H11a; 2.47, d,d, $J_{5a,4}$ 5.1Hz, $J_{5a,5b}$ 16.3Hz, H5a; 3.03, d,d, $J_{5b,4}$ 7.1Hz, $J_{5b,5a}$ 16.3Hz, H5b; 3.05, d,d, 3.10, d,d, ^3J 3.5Hz, $J_{2,7}$ 10.4Hz, (H2,H7); 3.39, m, H1,H8; 3.62, d,d, $J_{4,5a}$ 5.1Hz, $J_{4,5b}$ 7.1Hz, H4; 6.15, d,d, 6.21, d,d, ^3J 2.9Hz, ^3J 3.0Hz, $J_{9,10}$ 5.6Hz, (H9,H10); 7.08, m, 2H, 7.25, m, 3H, phenyls. ^{13}C n.m.r. δ_C 43.1, 47.0, 47.7, 48.6, 50.5, 51.6, 53.2, (H1,H2,H4,H5,H7,H8,H11); 127.2 (2C), 127.5, 128.9 (2C), phenyl carbons; 135.9, ipso phenyl carbon; 136.0, 136.9, (C9,C10); 208.5, 209.3, (C3,C6) (Found: $M^{+\cdot}$, 252.1142; C, 80.6; H, 6.3. $C_{17}H_{16}O_2$ requires: $M^{+\cdot}$, 252.1150; C, 80.9; H, 6.4%). Further elution gave endo-3-hydroxy-3,4-diphenyl[6,2,1,$0^{2,7}$]undec-9-ene-6-one

(120) (0.78 g) which was recrystallised from ethanol-dichloromethane as colourless prisms, m.p. 183-186°. ν_{max} 3000, 1705 cm^{-1}. ^{1}H n.m.r. δ_H 1.37, d, $J_{11b,11a}$ 8.5Hz, H11b; 1.48, br d, $J_{11a,11b}$ 8.5Hz, H11a; 2.54, m, H8; 2.67, d,d, $J_{4a,5}$ 10.4Hz, $J_{4a,4b}$ 18.4Hz, H4a; 2.76, d,d, $J_{4b,5}$ 8.1Hz, $J_{4b,4a}$ 18.4Hz, H4b; 3.29, d,d, 3.34, d,d, ^{3}J 2.9Hz, ^{3}J 3.2Hz, $J_{2,7}$ 11.6Hz, (H2,H7); 3.35, m, H1; 3.67, d,d, $J_{5,4b}$ 8.1Hz, $J_{5,4a}$ 10.4Hz, H5; 6.25, d,d, $J_{10,1}$ 3.0Hz, $J_{10,9}$ 5.6Hz, H10; 6.58, d,d, $J_{9,8}$ 3.0Hz, $J_{9,10}$ 5.6Hz, H9; 7.0-7.3, m, 10H, phenyls. ^{13}C n.m.r. δ_C 44.0 (2C), 44.7, 50.7, 51.2, 52.5, 54.6, (C1,C2,C4,C5,C7,C8,C11); 77.8, C6; 125.1 (2C), 126.0, 126.1, 127.6 (4C), 128.8 (2C), phenyl carbons; 131.9, C10; 140.2, C9; 140.6, 144.6, ipso phenyl carbons; 211.1 C3 (Found: $M^{+}\cdot$, 330.1626; C, 83.3; H, 6.8. $C_{23}H_{22}O_2$ requires: $M^{+}\cdot$, 330.1620; C, 83.6; H, 6.7%).

ii) The reaction of adduct **(8e)** (1.0 g, 4.46 mmol) with phenyl magnesium bromide required magnesium turnings (1.08 g, 45.0 mmol) and bromobenzene (4.7 ml, 44.6 mmol) was performed as above. Following workup and absorption of the crude reaction mixture onto silica, elution with petroleum ether gave biphenyl (0.17 g). Elution with ether-petroleum ether (1:9) gave 3,10-dihydroxytetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]pentadeca-2,4,6,8,10-pentaene **(122)** (0.14 g) as above. Elution with ether-petroleum ether (1:1) gave <u>endo</u>-3-hydroxy-3-phenyltetracyclo[10,2,1,$0^{2,11}$,$0^{4,9}$]pentadeca-4,6,8,13-tetraene-10-one **(127)** (0.89 g) as an oil or semi-crystalline solid. ν_{max} 3450, 3000, 1670 cm^{-1}. ^{1}H n.m.r. δ_H 1.45, d, $J_{15b,15a}$ 8.6Hz, H15b; 1.49, d, $J_{15a,15b}$ 8.6Hz, H15a; 3.28, d,d, 3.32, d,d, ^{3}J 3.5Hz, $J_{2,11}$ 9.0Hz, (H2,H11); 3.32, m,

3.40, m, (H1,H12); 5.23, d,d, 5.75, d,d, J 2.7Hz, J 2.9Hz, $J_{13,14}$ 5.8Hz, (H13,H14); 7.25, m, 6H 7.56, m, 2H, 7.68, m, 1H, (phenyls, H5,H6,H7,H8). ^{13}C n.m.r. δ_C 46.9, 49.8, 49.9, 50.9, 51.0, (C1,C2,C11,C12,C15); 75.0, C6; 125.0, 125.2 (2C), 125.6, 127.3, 127.5, 128.6 (2C), 131.1, (phenyl carbons,C5,C6,C7,C8); 134.1, 134.5, (C13,C14); 134.9, 145.8, 149.6, (ipso phenyl carbon,C4,C9); 201.0, C3 (Found: $M^{+\cdot}$, 302.1312. $C_{21}H_{18}O_2$ requires: $M^{+\cdot}$, 302.1307).

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